

## Upper and Lower Bounds on $s$ -Wave Electron-Hydrogen Scattering. I\*

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A uniform method of determining upper and lower bounds on phase shifts is presented for three-body problems in the case that two of the particles are identical, by taking  $s$ -wave triplet  $e^-$ -H scattering as a model. The method of evaluation of the upper bound involves replacing an effective optical potential by its separable lower bound in the integrodifferential equation, which is then solved numerically. At this state of the calculation an error of 20%, at the maximum, is reported. Variational methods for the improvement of this calculation and potentialities of this approach for the study of  $e^-$ -H scattering in the inelastic region are discussed.

### I. INTRODUCTION

A great amount of insight into the collision problems has been achieved in recent years by the development of methods of obtaining bounds.<sup>1,2</sup> Inability to solve the problem exactly has led the theorist to formulate upper- and lower-bound principles on quantities of interest in order to understand the experimental results. In the case of the simplest unsolved three-body problem of  $e^-$ -H scattering, the most outstanding contributions on the lower bound are those of Spruch and his collaborators,<sup>3</sup> although others have also made significant contributions.<sup>4,5,6,7,8</sup> Schwinger's variational principle also yields a lower bound. More recently, Sugar and Blankenbecler<sup>9</sup> have given a uniform method of finding both upper and lower bounds, but have applied it only to simplified examples. The aim of this paper is to develop and illustrate such a method for a model three-body problem including the possibilities of exchange effects.

As a model, we have chosen to determine upper and lower bounds on  $s$ -wave  $e^-$ -H scattering in the triplet state. The theory of electron-hydrogen scattering has been widely discussed in the literature, and our approach should be contrasted with the work of Spruch,<sup>3</sup> calculations by Temkin,<sup>4</sup> a study of the structure of resonances below the inelastic threshold by Chen,<sup>10</sup> and the optical-potential approach of Feshbach.<sup>11</sup> To find the upper bound on the phase shift we replace an effective optical potential by a lower-bound separable potential. In the theoretical discussion, we derive the theorems on bounds and methods to improve the bounds by Schwartz inequalities. In particular, we write down the equation to improve the upper-bound phase shift by dealing with the neglected part of the effective optical potential by the variational method. In actual treatment of the problem, we do not employ trial functions to calculate the phase shifts from variational expressions.<sup>9</sup> Instead, we write down the upper- and lower-bound integrodifferential equations, by choosing a symmetric projection operator  $P$  to include exchange effects, and solve them numerically.

In Sec. II we define the operators and boundary conditions and settle the questions of notation.

In Sec. III we discuss variational principles for a three-particle system when two of the particles are identical, and discuss improvable bounds. The equations of triplet  $s$ -wave scattering in the  $e^-$ -H scattering example are presented and solved in Sec. IV, while Sec. V is devoted to discussion of results.

Two outstanding results emerge from the present treatment of the problem: (i) In the triplet  $s$ -wave  $e^-$ -H scattering, Pauli's principle plays an important role. We find that exchange effects in low-energy scattering are more important than virtual excitations of the hydrogen atom to higher states. (ii) The maximum theoretical error at energies reasonably close to the nonintegrable singularity in the optical potential is about 20% and stands to be improved by methods discussed in the text. We feel this study provides a test of the suitability of our kind of variational method for predicting the behavior of the phase shift in the region of the lowest inelastic threshold—an unsolved scattering problem of extreme complexity.

### II. DEFINITIONS

The  $s$ -wave scattering of electrons from hydrogen is described by the Schrödinger equation with zero total angular momentum for two electrons in the field of an infinitely heavy nucleus carrying a unit positive charge. Such an equation can be reduced to the following partial-differential equation<sup>4,12</sup>:

$$\left[ -\frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 - \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 - \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right. \\ \left. \times \frac{1}{\sin\theta_{12}} \frac{\partial}{\partial \theta_{12}} \sin\theta_{12} \frac{\partial}{\partial \theta_{12}} \right. \\ \left. - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} - E \right] f(r_1 r_2 \theta_{12}) = 0$$

in rydbergs. In the Hamiltonian, two-body interactions are included, while the three-body interactions have been neglected. Writing

$$r_1 r_2 f(r_1 r_2 \theta_{12}) = \Psi(r_1 r_2 \theta_{12}),$$

we have the equation

$$\left[ -\frac{\partial^2}{\partial r_1^2} - \frac{\partial^2}{\partial r_2^2} - \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right. \\ \left. + V_1(r_1) + V_2(r_2) + V_{12}(r_1 r_2) - E \right] \Psi(r_1 r_2 \theta_{12}) = 0, \quad (2.1)$$

where  $V_1(r_1) = -2/r_1$ ,  $V_2(r_2) = -2/r_2$ , and  $V_{12}(r_1 r_2) = 2/r_{12}$

The eigenfunctions of the angle-dependent operator in the above equation are the Legendre polynomials

$$\frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \sin \theta_{12} \frac{\partial}{\partial \theta_{12}} P_l(\cos \theta_{12}) \\ = -l(l+1) P_l(\cos \theta_{12}).$$

Under exchange,  $\vec{r}_1 \rightleftharpoons \vec{r}_2$ , the three coordinates of the  $s$ -wave problem transform according to  $r_1 \rightleftharpoons r_2$  and  $\theta_{12} \rightleftharpoons \theta_{12}$ . The Hamiltonian operator, being invariant under the interchange of particle identities, then admits solutions which are symmetric and anti-symmetric, or singlet and triplet in the present case, having the properties

$$\Psi^\pm(r_1 r_2 \theta_{12}) = \pm \Psi^\pm(r_2 r_1 \theta_{12}) \quad (2.2)$$

The boundary conditions on the scattered particle at energies below the inelastic threshold are such that  $\Psi(r_1 r_2 \theta_{12})$  satisfies

$$\Psi(r_1 r_2 \theta_{12}) \sim U_{10}(r_1) \sin(kr_2 + \delta) \quad (2.3)$$

as  $r_2 \rightarrow \infty$ , where  $U_{10}(r_1)$  is  $r_1$  times the ground-state wave function of the hydrogen atom.

We introduce a pair of projection operators  $P$  and  $Q$  which project out orthogonal parts of the Hilbert space.<sup>13</sup> Then

$$P + Q = 1, \quad P^2 = P, \quad Q^2 = Q,$$

and the following coupled equations are obtained from the Schrödinger equation

$$P(H-E)(P+Q)\Psi = 0, \quad Q(H-E)(P+Q)\Psi = 0,$$

which we can formally solve for  $Q\Psi$ :

$$Q\Psi = \frac{1}{Q(E-H)Q} QHP\Psi,$$

obtaining for  $P\Psi$

$$[PHP + PHQ \frac{1}{E-QHQ} QHP - E]P\Psi = 0. \quad (2.4)$$

The Hamiltonian operator  $H$  has already been defined in coordinate space; now we shall define the

projection operators  $P$  and  $Q$ . Since we wish to take into account the identity of the two electrons, the projection operator  $P$  must be symmetric under interchange of indices 1 and 2. Secondly,  $P\Psi$  should give the correct asymptotic behavior for energies below the inelastic threshold, i. e.,

$$P\Psi \sim \Psi \quad (2.5)$$

as  $r_1$  or  $r_2 \rightarrow \infty$ . A pair of projection operators satisfying the above conditions are

$$Q = Q_1 Q_2 \quad \text{and} \quad P = 1 - Q, \quad (2.6)$$

where  $Q_1 = 1 - P_1$  and  $P_1$  is the projection operator which projects out the hydrogenic ground state in the coordinates of the electron carrying the index 1. The above choice insures that the two electrons will never be in the ground state at the same time. From (2.6), the operator  $P$  is

$$P = P_1 + P_2 - P_1 P_2,$$

where we chose

$$P_1 = \int |1(1) r_2\rangle \langle r_2 1(1)| dr_2, \\ P_2 = \int |1(2) r_1\rangle \langle r_1 1(2)| dr_1. \quad (2.7)$$

Integration over the angles  $\theta_{12}$  is also implied by the integral sign. Note that

$$\langle r_2 | r_2' \rangle = \delta(r_2 - r_2'), \\ \langle 1(1) | r_1 \rangle = U_{10}(r_1) = \sqrt{2} r_1 e^{-r_1} P_0(\cos \theta_{12}). \quad (2.8)$$

For the antisymmetric function  $\Psi^-$ , the following relations hold:

$$\int \langle r_2 1(1) | \Psi^- \rangle dr_2 = \Phi^-(r_2), \\ \int \langle r_1 1(2) | \Psi^- \rangle dr_1 = -\Phi^-(r_1). \quad (2.9)$$

Hence, in coordinate representation,  $P\Psi^-$  is

$$P\Psi^- = \langle r_1 | 1(1) \rangle \Phi^-(r_2) - \langle r_2 | 1(2) \rangle \Phi^-(r_1). \quad (2.10)$$

It satisfies the boundary condition (2.5), and according to (2.3),

$$\Phi^-(r) \sim \sin(kr + \delta^-) \quad \text{as} \quad r \rightarrow \infty$$

and  $\Phi^-(0) = 0$  (2.11)

is also required. Define

$$PHQ \frac{1}{E-QHQ} QHP \equiv W_Q.$$

If we project onto the ground state of one of the particles, Eq. (2.4) is an integrodifferential equation in the variable of the other particle. Neglecting the energy-dependent potential  $W_Q$ , the exact solution of this equation gives a lower bound on the phase shift (we shall prove the bound principle later in the section). If, in the energy-dependent denominator of  $W_Q$ , we replace the Hamiltonian operator  $QHQ$  by a lower-bound value of its lowest

binding energy ( $E_L$ ) and include the non-separable term  $W_Q$  in the integrodifferential equation, then we state that the solution would yield an upper or lower bound if the separable  $W_Q$  is positive or negative definite in the energy range of interest. In the case where all three particles are distinguishable, the integrodifferential equations reduce to

differential equations, and the nature of the bounds on the phase shift is well known.<sup>9</sup> But if two of the particles are indistinguishable, and the equations are no longer second-order differential equations, then proofs of the variational character of the phase shifts on effective potentials should be given. This we accomplish in the following section.

### III. VARIATIONAL PRINCIPLES

The operator equation

$$P_1(PHP - E)P\Psi^- = 0 \quad (3.1a)$$

written out in coordinate representation reads

$$\begin{aligned} (d^2/dr_2^2 + k_0^2)\Phi^-(r_2) &= V_2(r_2)\Phi^-(r_2) + \langle U_{10}(r_1') | V_{12}(r_1', r_2) | U_{10}(r_1') \rangle \Phi^-(r_2) \\ &- \langle U_{10}(r_1') | V_{12}(r_1', r_2) | \Phi^-(r_2') \rangle U_{10}(r_2), \end{aligned} \quad (3.1b)$$

where  $k_0^2 = E + 1$  in rydbergs. Using the zero-partial-wave Green's function defined by

$$(d^2/dr_2^2 + k_0^2)g_{10}(r_2, r_2') = \delta(r_2 - r_2'),$$

we can formally write the solution of (3.1b) as

$$\begin{aligned} U_{10}(r_1)\Phi^-(r_2) &= U_{10}(r_1)\omega_0(k_0r_2) + \int_{-1}^{+1} \int_0^\infty dz_{12} dr_1' dr_2' g_0(r_2, r_2') U_{10}(r_1) \\ &\times U_{10}(r_1') [V_2(r_2') + V_{12}(r_1' r_2')] [U_{10}(r_1')\Phi^-(r_2') - U_{10}(r_2')\Phi^-(r_1')], \end{aligned} \quad (3.2)$$

where

$$g_0(r_2, r_2') = k_0^{-1} \omega_0(k_0r_{2<}) v_0(k_0r_{2>}), \quad \omega_0(k_0r_2) = k_0r_2 j_0(k_0r_2), \quad v_0(k_0r_2) = k_0r_2 n_0(k_0r_2), \quad \text{and } \cos\theta_{12} = z_{12}.$$

In the limit  $r_2 \rightarrow \infty$ , the phase shift is defined by

$$\Phi(r_2) \sim \omega_0(k_0r_2) - \tan\delta_0^- v_0(k_0r_2), \quad (3.3)$$

and turns out to be

$$\tan\delta_0^- = -k_0^{-1} \int_{-1}^{+1} \int_0^\infty dz_{12} dr_1' dr_2' U_{10}(r_1') \omega_0(k_0r_2') [V_2(r_2') + V_{12}(r_1' r_2')] [U_{10}(r_1')\Phi^-(r_2') - U_{10}(r_2')\Phi^-(r_1')]. \quad (3.4)$$

The limit at infinity and the definition of  $\tan\delta_0^-$  would stay the same if we were to start with the equation

$$\begin{aligned} U_{10}(r_1)\Phi^\pm(r_2) \pm U_{10}(r_2)\Phi^\pm(r_1) &= U_{10}(r_1)\omega_0(k_0r_2) \\ &+ \int_{-1}^{+1} \int_0^\infty dz_{12} dr_1' dr_2' g_0(r_2, r_2') U_{10}(r_1) U_{10}(r_1') [V_2(r_2') + V_{12}(r_1' r_2')] [U_{10}(r_1')\Phi^\pm(r_2') \pm U_{10}(r_2')\Phi^\pm(r_1')]. \end{aligned} \quad (3.5)$$

The positive sign refers to the spatially symmetric wave function. For a proof that this is the correct integral equation for elastic scattering from the hydrogen atom in its ground state, we refer the reader to Wu and Ohmura.<sup>14</sup> The difference between their Hamiltonian and our definition in (2.1) should be kept in mind. The only angular dependence in our equations comes through  $\theta_{12}$ , and under the interchange of particle labels,  $r_1 \rightleftharpoons r_2$ , it transforms as  $\theta_{12} \rightleftharpoons +\theta_{12}$ . Also our Green's function is real.

Though in what follows we will restrict our derivations to elastic scattering in the lowest channel, generalization to other channels is obvious.<sup>9</sup> It is convenient to introduce the reactance matrix by

$$\tan\delta_0^\pm = -k_0^{-1} \langle \chi | U_2 | \Psi_0^\pm \rangle = K_0^\pm, \quad (3.6)$$

where  $\chi = U_{10}(r_1)\omega_0(kr_2)$ ,  $U_2 = V_2(r_2) + V_{12}(r_1 r_2)$ , and  $\Psi_0^\pm = U_{10}(r_1)\Phi^\pm(r_2) \pm U_{10}(r_2)\Phi^\pm(r_1)$ . The formal solution of (3.5) is

$$|\Psi_0^\pm\rangle = (1 - G_{10}U_2)^{-1} |\chi\rangle = R|\chi\rangle, \quad (3.7)$$

where  $G_{10} = g_0(r_2, r_2') U_{10}(r_1) U_{10}(r_1')$ . The reactance matrix becomes

$$K_0^\pm = -k_0^{-1} \langle \chi | U_2 R | \chi \rangle, \quad (3.8)$$

and the resolvent exists because the Green's function involves one free and one interacting particle.

In order to establish bounds on the phase shift, we are led to examine its dependence on the potential. Suppose that  $U_2$  depends upon a parameter  $\lambda$ ; then differentiation of (3.8) with respect to  $\lambda$  yields

$$(d/d\lambda)\delta^\pm(\lambda) = -k_0^{-1} \cos^2\delta^\pm(\lambda) \langle \chi | R(\lambda) [dU_2(\lambda)/d\lambda] R(\lambda) | \chi \rangle = -k_0^{-1} \cos^2\delta^\pm(\lambda) \langle \Psi_0^\pm(\lambda) | [dU_2(\lambda)/d\lambda] | \Psi_0^\pm(\lambda) \rangle, \quad (3.9)$$

which shows that the phase shift is monotonic in the potential.  $\Psi_0^\pm(\lambda)$  is the exact solution of (3.7). Now choose

$$U_2(\lambda) = U_2'' + \lambda(U_2' - U_2''),$$

with  $U_2' \geq U_2''$ . Then we find, upon integrating (3.9),

$$\delta^\pm(1) - \delta^\pm(0) = -k_0^{-1} \int_0^1 d\lambda \cos^2\delta(\lambda) \langle \Psi_0^\pm(\lambda) | U_2' - U_2'' | \Psi_0^\pm(\lambda) \rangle \leq 0. \quad (3.10)$$

Thus, the larger (more repulsive) the potential the smaller the phase shift. For attractive potentials the inference should be reversed. Hence, to "bound" the phase shift one has only to write smaller and larger solvable potentials than the original. The techniques for doing this are already available.<sup>9</sup> In the following, the techniques of Sugar and Blankenbecler are extended and applied to the three-body problem with two identical particles.

For a positive definite  $U_2$ , Schwarz's inequality says that

$$U_2 \geq U_2 | q \rangle \langle \langle q | U_2 | q \rangle \rangle^{-1} \langle q | U_2 \equiv U_S,$$

where  $\langle q |$  and  $| q \rangle$  are column and row vectors made up of an arbitrary set  $F_i$  of trial functions. A function from the set  $F_i$  is of the form

$$F_i^\pm(r_1, r_2) = U_{10}(r_1) f_i^\pm(r_2) \pm U_{10}(r_2) f_i^\pm(r_1).$$

The phase shift for the potential  $U_S$  is given by

$$\tan \delta_0^S = -k_0^{-1} \langle \chi | U_2 | q \rangle \langle \langle q | U_2 - U_2 G_{10} U_2 | q \rangle \rangle^{-1} \langle q | U_2 | \chi \rangle \quad (3.11)$$

in matrix notation. This expression for the phase shift is the same as the Schwinger's variational principle for the two-body scattering. For  $U_2 \geq 0$ , (3.11) is a minimum principle and  $\delta_0^S \geq \delta_0$ , while for  $U_2 \leq 0$ , (3.11) is a maximum principle and  $\delta_0^S \leq \delta_0$ . The phase-shift bound is always improved if the number of trial functions  $F_i$  in the set is increased. If in the set  $F_i$ , one of the  $f_i$ 's turns out to be equal to  $\Phi$ , then the phase shift given by (3.11) is exact.

In Eq. (3.9) we have derived the variation of the phase shift with respect to a variation of the nonsymmetric interaction potential  $U_2(r_1, r_2)$ . It would also be interesting to see how the phase shift behaves as the symmetric potential  $V_{12}(r_1, r_2)$  in the exchange term in (3.1b) is varied. Writing Eq. (3.1b) with the aim of treating the exchange term as the interaction, we have

$$[d^2/dr_2^2 + k_0^2 + (2/r_2) e^{-2r_2} + 2e^{-2r_2}] \Phi^-(r_2) = -\langle U_{10}(r_1') | V_{12}(r_1', r_2) | \Phi^-(r_1') \rangle U_{10}(r_2), \quad (3.12)$$

where we have used the expansion

$$V_{12}(r_1, r_2) = 2 \sum_{l=0}^{\infty} \frac{r < l}{r_2^{l+1}} P_l(\cos \theta_{12})$$

and integrated over the angle  $\theta_{12}$ . Also consider the equation

$$[d^2/dr_2^2 + k_0^2 + (2/r_2) e^{-2r_2} + 2e^{-2r_2}] \Phi_1^-(r_2) = -\langle U_{10}(r_1') | V_{12}'(r_1', r_2) | \Phi_1^-(r_1') \rangle U_{10}(r_2), \quad (3.13)$$

where a perturbed  $V_{12}'$  would produce a corresponding change in the boundary condition in the wave function at infinity, such that

$$\Phi_1^-(r_2) \sim \sin(kr_2 + \delta_1^-) \quad (3.14)$$

as  $r_2 \rightarrow \infty$ . Then it is easy to verify that

$$\int \int \int U_{10}(r_1) \Phi_1^-(r_2) [V_{12}(r_1, r_2) - V_{12}'(r_1, r_2)] \Phi_1^-(r_1) U_{10}(r_2) dr_1 dr_2 dz_{12} = k_0 (\tan \delta_0^- - \tan \delta_1^-). \quad (3.15)$$

Now by introducing a parameter  $\lambda$  in  $V_{12}$  and proceeding as before, we obtain

$$(d/d\lambda)\delta_0^-(\lambda) = [\cos^2\delta_0^-(\lambda)/k_0] \int \int \int dr_1 dr_2 dz_{12} U_{10}(r_1) \Phi_{\lambda}^-(r_2) (dV_{12}/d\lambda) \Phi_{\lambda}^-(r_1) U_{10}(r_2), \quad (3.16)$$

a result which takes into account Fermi statistics in the triplet s-wave electron-hydrogen scattering. From (3.16) it is possible to obtain an analog of (3.10), but with a positive sign, implying that, for the repulsive interaction potential  $V_{12}$ , the exclusion of the exchange term would give a lower bound on the phase shift, while inclusion would improve it. This is borne out by the results quoted in Ref. 1.

Before we conclude this section we would like to mention possible methods for improving the bound mentioned at the end of the last section. For purposes of this discussion we shall restrict the scattering to energies below the first inelastic threshold. The energy-dependent potential  $W_Q$  is negative definite in this energy range. Thus, omitting  $W_Q$ , the solution of the equation (2.4) for the phase shift gives a lower bound. However, if  $W_Q$  is reinstated in the equation but with  $QHQ$  replaced by its lower bound in energy ( $E_L$ ), then the solution will yield an upper bound on the phase shift. We have evaluated a lower bound and an upper bound for a particular choice of  $E_L$  in the next section. The upper bound at this stage is by no means the final word in achievable accuracy. It can be improved at the first stage by improving the lower bound on the lowest-energy eigenvalue  $E_L$  of the Hamiltonian  $QHQ$ . A number of methods are available in the literature for this purpose.<sup>15,16</sup> At the next stage one turns to the methods of Schwarz's inequality discussed in this section.

In order to improve the upper bound at the next stage, let us pick up the potential term which we left out of Eq. (2.4). This term is

$$(E - QHQ)^{-1} - (E - E_L)^{-1} \equiv V_Q,$$

and we assume that it is multiplied from the left by the operator  $PHQ$  and from the right by  $QHP$ . For the scattering energies below the first inelastic threshold,  $V_Q$  is positive definite. Hence by Schwarz's inequality

$$V_Q \geq V_{Qs} \equiv \frac{V_Q |q\rangle \langle q| V_Q}{\langle q| V_Q |q\rangle} = (E - E_L)^{-1} (E_L - QHQ) |p\rangle [\langle p| (E_L - QHQ) (E - QHQ) |p\rangle]^{-1} \langle p| (E_L - QHQ). \quad (3.17)$$

[Here we have defined a new trial function  $|p\rangle = (E - QHQ)^{-1} |q\rangle$ . The improved upper-bound phase shift  $\delta^u$  is given by the equation

$$\begin{aligned} \tan(\delta^u - \delta_0^u) &= k_0^{-1} \cos^2 \delta_0^u \langle \Psi_0^u | (E_L - QHQ) |p\rangle [(E - E_L) \langle p| (E_L - QHQ) (E - QHQ) |p\rangle \\ &\quad + \langle p| (E_L - QHQ) G_0^u (E_L - QHQ) |p\rangle]^{-1} \langle p| (E_L - QHQ) | \Psi_0^u \rangle, \end{aligned} \quad (3.18)$$

where  $G_0^u$  is the Green's function formed out of the regular  $\Psi_0^u$  and the irregular  $\Psi_0^u$  solutions of the original equation for the upper bound  $\delta_0^u$ .

#### IV. UPPER- AND LOWER-BOUND EQUATIONS AND NUMERICAL EVALUATIONS

In Eq. (3.1b), integration over the angle  $\theta_{12}$  can be performed trivially, as only the  $l=0$  term in the partial-wave expansion of  $V_{12}$  gives the nonzero contribution. The equation for the lower bound is then

$$[d^2/dr^2 + (2/r)e^{-2r} + 2e^{-2r} + k_0^2] \Phi^-(r) = -8e^{-r} [I(r) + J(r)], \quad (4.1)$$

where  $I(r) = \int_0^r r' e^{-r'} \Phi^-(r') dr'$ ,  $J(r) = r \int_r^\infty e^{-r'} \Phi^-(r') dr'$ .

For the upper bound, we have to add the term

$$-P_1 H Q \frac{1}{E - E_L} Q H P \Psi^- = \frac{1}{E - E_L} (P_1 V_{12} P V_{12} P - P V_{12}^2 P) \Psi^-$$

to Eq. (3.1).

Written out more explicitly it appears as

$$\begin{aligned} &= (E - E_L)^{-1} [F^2(r_2) \Phi^-(r_2) - F(r_2) \langle r_2 | 1(2) \rangle \langle 1(1) | r_1' \rangle V_{12}(r_1', r_2) \Phi^-(r_1') - F(r_2) \langle r_2 | 1(2) \rangle \langle 1(1) | r_1'' \rangle \\ &\quad \times \langle r_1'' | 1(1) \rangle \langle 1(2) | r_2' \rangle V_{12}(r_1'', r_2') \Phi^-(r_2') + F(r_2) \langle r_2 | 1(2) \rangle \langle 1(1) | r_1'' \rangle F(r_1'') \Phi^-(r_1'') + \langle r_2 | 1(2) \rangle \langle 1(1) | r_1'' \rangle \\ &\quad \times V_{12}(r_1'', r_2) \langle r_1'' | 1(1) \rangle \langle 1(2) | r_2' \rangle V_{12}(r_1'', r_2') \Phi^-(r_2') - \langle r_2 | 1(2) \rangle \langle 1(1) | r_1'' \rangle V_{12}(r_1'', r_2) F(r_1'') \Phi^-(r_1'') \\ &\quad - \langle 1(1) | V_{12}^2(r_1, r_2) | 1(1) \rangle \Phi^-(r_2) + \langle r_2 | 1(2) \rangle \langle 1(1) | r_1' \rangle V_{12}^2(r_1', r_2) \Phi^-(r_1')], \end{aligned} \quad (4.2)$$

where we have dropped a factor of  $U_{10}(r_1)$ . Though we have not indicated it by integral signs, repeated variables are meant to be integrated over. We have defined

$$\langle 1(1) | V_{12} | 1(1) \rangle \equiv F(r_2).$$

Completing the angular integrations in (4.2) and adding this term to the left-hand side of equation (4.1), we have the equation for the upper bound:

$$\begin{aligned}
 & \left[ \frac{d^2}{dr^2} + k_0^2 + \frac{2F_1(r)}{r} + \frac{4Q^2}{E-E_L} + \frac{8}{r(E-E_L)} \int_0^\infty dr' (r'e^{-2r'} - re^{-2r}) \ln \left| \frac{r'-r}{r'+r} \right| \right] \Phi^-(r) \\
 & = -8e^{-r} [I(r) + J(r)] + \frac{16e^{-r}}{E-E_L} \left[ \frac{Q(r)}{r} [I(r) + J(r)] - 4 \left\{ \int_0^r r' e^{-2r'} [I(r') + J(r')] dr' + r \int_r^\infty e^{-2r'} [I(r') + J(r')] dr' \right. \right. \\
 & \quad \left. \left. - Q(r) \int_0^\infty r' e^{-2r'} [I(r') + J(r')] dr' \right\} + \int_0^r Q(r') e^{-r'} \Phi^-(r') dr' + r \int_r^\infty \frac{Q(r') e^{-r'}}{r'} \Phi^-(r') dr' \right. \\
 & \quad \left. - Q(r) \int_0^\infty e^{-r'} Q(r') \Phi^-(r') dr' + \frac{1}{2} \int_0^\infty dr' [\Phi^-(r') e^{-r'} - \Phi^-(r) e^{-r}] \ln \left| \frac{r'-r}{r'+r} \right| \right], \quad (4.3)
 \end{aligned}$$

where  $F_1(r) = (1+r)e^{-2r}$ ,  $Q(r) = 1 - F_1(r)$ . Note the subtraction and addition of the term

$$8(E-E_L)^{-1} e^{-2r} \Phi^-(r) \int_0^\infty dr' \ln \left| \frac{r'-r}{r'+r} \right|$$

to remove the logarithmic singularity.

The lower bound  $E_L$  was chosen from Ref. 3, which gives  $E_L = -0.36111$  Ry. The manipulation needed to integrate Eqs. (4.1) and (4.3) numerically by direct iterations is to integrate formally the equations twice, resulting in

$$\Phi^-(r) = \int_0^r dr' (1 - \int_0^{r'} ds \{ [k_0^2 + M(s)] \Phi^-(s) + N(s) \}) , \quad (4.4)$$

where the boundary conditions on  $\Phi^-$ ,  $\Phi^-(0) = 0$ , and  $\Phi^{-\prime}(0) = 1$ , are evident. The function  $N$  contains the terms having  $\Phi^-$  under the integral sign and  $M$  contains the terms multiplying  $\Phi^-$ . For the simpler Eq. (4.1),

$$M(s) = (2/s)e^{-2s} + 2e^{-2s}, \quad N(s) = 8e^{-s} [I(s) + J(s)] .$$

Equations (4.1) and (4.4) were solved by direct iteration, and it was found that convergence was greatly enhanced if input at any stage of the iteration was formed by properly weighting input and output functions at the previous stage. The most suitable weights were determined by trial. Though only one weight proved appropriate for all values of  $k_0$  for the lower-bound Eq. (4.1), it varied for different values of  $k_0$  for the upper-bound equation. For values of  $k_0 = 0.7$  and  $0.73$  close to the nonintegrable singularity in Eq. (4.3), the convergence becomes difficult, and the input function at any stage equaled 0.1 times the output function plus 0.9 times the input function at the last stage of iteration. The number of iterations required for convergence was about 50.

A double-difference integral formula with an accuracy of better than 1 part in  $10^4$  was employed. The accuracy demanded of  $\Phi^-(r)$  was such that, at any stage of iteration, values of the input and output functions were required to agree to four places at the five end points. To determine the phase shift, a subroutine was called to give us the argument of the complex function  $(\Phi^-(r), \Phi^{-\prime}(r)/k_0)$ . The phase shift was thus determined as a function of distance  $r$  by subtracting  $k_0 r$  from the real argument. It was observed that the phase-shift function practically became constant at  $r \approx 2$ , doing away with the necessity of integrating the equations to infinity. Thus the equations were integrated out to  $r = 12.3$  as the point at infinity, and the phase shift was picked up at  $r = 11$  where the solution  $\Phi^-(r)$  showed even better than fourth place convergence. The inaccuracy of this approximation was more pronounced at small values of  $k_0$ . This is borne out by the investigations of Temkin and Sullivan.<sup>17</sup>

In the iteration of the upper-bound equation, the term

$$C(\Phi^-(r)) = \int_0^\infty dr' [e^{-r'} \Phi^-(r') - e^{-r} \Phi^-(r)] \ln \left| \frac{r'-r}{r'+r} \right| \quad (4.5)$$

was treated in a special way. To begin with, the lower-bound wave function  $\Phi_0^-(r)$  was used to evaluate  $C$ , giving the value  $C_0$ , and a solution  $\Phi_1^-(r)$  of Eq. (4.3) was obtained. Then an improved  $C$  called  $C_1$  was evaluated by using  $\Phi_1^-(r)$  in (4.5), and again Eq. (4.3) was iterated for  $\Phi_2^-(r)$ , and so on. The phase shift was obtained by observing a converging sequence. A typical case of this sequence for  $k_0 = 0.3$  is given in Table I.

TABLE I. Upper-bound phase shifts in radians for successive approximations of the term (4.5) for  $k_0=0.3$ .

	$C_0$	$C_1$	$C_2$
$\delta_0^u$	2.557 42	2.556 06	2.556 31

### V. DISCUSSION

The pertinent theoretical calculations to compare our results with are available in the work of Temkin and Sullivan.<sup>17</sup> Their results are quoted in Table II and plotted in Fig. 1 along with ours. They are seen to lie nicely between our upper and lower bounds. Since our aim is to explicitly bring out the maximum theoretical error involved in variational calculations of this nature, we proceed by adopting a definition of the maximum error in our theory.

For the purpose of this discussion we define

$$W_L \equiv PHQ \frac{1}{E - E_L} QHP,$$

where  $W_L$  is the lower bound on the negative-definite part of the optical potential. The lower bound on the potential leads in turn to the upper bound  $\delta^u$  on the phase shift. By our choice of the lower bound on energy  $E_L$ , the nonintegrable singularity in  $W_L$  occurs at  $k_0^2=0.63999$ . We notice that as the value of  $k_0^2$  approaches this singularity, the difference between the bound curves increases gradually. We define the maximum theoretical error as the difference between upper- and lower-bound phase shifts at a value of  $k_0^2$  that is 0.15 Ry away from the singularity. At  $k_0^2=0.49$ , the maximum error is about 20%, and it increases for higher  $k_0^2$ .

This result can be improved considerably by the methods detailed in Sec. III. Thus we assert that ours is a practical method for studying the energy dependence of the phase shift in the first inelastic region. We shall describe briefly how this can

TABLE II. Triplet  $s$ -wave  $e^-$ -H scattering phase shifts in radians;  $\delta_0^u$ , upper bound;  $\delta_0$ , lower bound. The numbers in parentheses give the maximum uncertainties in the last digit quoted.

$k_0$	$\delta_0^L$	$\delta_0^u$	Temkin and Sullivan ( $\delta$ )
0.1	2.907(1)	2.953(1)	2.9390
0.3	2.459(1)	2.556(1)	2.4996
0.4	2.255(1)	2.370(1)	2.2936
0.5	2.066(1)	2.216(2)	2.1052
0.6	1.896(1)	2.115(3)	1.9335
0.7	1.742(1)	2.141(4)	1.7801
0.73	1.700(1)	2.281(8)	

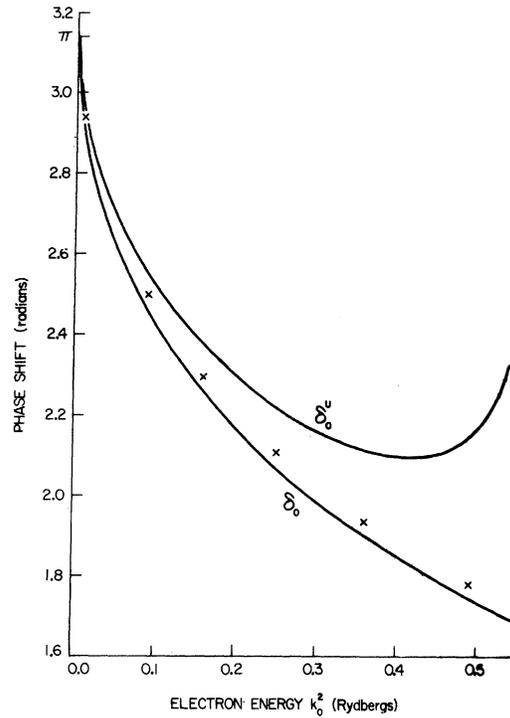


FIG. 1.  $s$ -wave  $e^-$ -H scattering in the triplet state. Upper-bound ( $\delta_0^u$ ) and lower-bound ( $\delta_0$ ) phase shifts. For comparison, Temkin and Sullivan's calculated results are indicated by  $\times$ 's.

materialize in the framework of our theory.

The lowest inelastic threshold occurs at  $k_0^2=0.703$ .<sup>18</sup> As the incident particle approaches the hydrogen atom, it is polarized by (induced) virtual transitions to excited states. The static approximation for the lower bound on the phase shift can be improved by taking into account the first few excited states of the hydrogen atom. For extensions of the study to energies in the first inelastic threshold, we have to include  $1s$ ,  $2s$ , and  $2p$  states of the hydrogen atom in the projection operator  $P$ . If the optical potential term in Eq. (2.4) is neglected, then this procedure is known as the close-coupling approximation and yields an improved lower bound on the phase shift. For the upper bound on the phase shift  $\delta^u$ , our method involves replacing the operator  $QHQ$  in the optical potential by its lower-bound energy. The choice of  $P$  in the present case indicates that  $QHQ$  is a Hamiltonian for which the two electrons are never in the  $1s$ ,  $2s$ , and  $2p$  states of the hydrogen atom at the same time. The crudest lower bound on the energy of  $QHQ$ , neglecting the repulsive interaction  $Q(1/r_{12})Q$  between the two electrons, is

$$E_L = -0.222 \text{ Ry.}$$

With this bound, the nonintegrable singularity in the operator  $W_L$  occurs at  $k_0^2=0.778$ , which is only 0.075 Ry further off from the point of inelastic

resonance. Our hope is that one would improve the lower-energy bound on  $QHQ$  by including the repulsive potential  $Q(1/r_{12})Q$  so that the difference between the singularity of  $W_L$  and the resonance would be more than 0.1 Ry, and the behavior of the phase shift in the region of the resonance could be determined.

The improvement of the reported upper bound, by an improved evaluation of  $E_L$  and with the  $1s-2s-2p$  projection (close-coupling approximation), will be the subject of a subsequent paper.

Inspection of Fig. 1 leads us to draw some interesting conclusions about the mechanism of exchange of electrons in  $e^-$ -H scattering and the effect of virtual excitations to higher states of the hydrogen atom. It appears that virtual excitations to higher states are not as important as the exchange mechanism in the low-energy scattering region. Sugar<sup>15</sup> found that, in the case of no-exchange scattering,

the inclusion of virtual excitations by including the bound  $W_L$  of the optical potential drastically altered the zero-energy behavior of the phase shift. We find that once we include exchange, virtual excitations to higher states are not a dominant mechanism in  $s$ -wave triplet  $e^-$ -H scattering. The shift in phase at zero energies in the lower bound (due to exchange of electrons) is explicitly brought out by Eq. (3.15).

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