

ured  $\epsilon_0(\text{H}^0)$ . A more meaningful comparison, with calculations by Dalgarno and Griffing<sup>20</sup> was shown in a previous publication, but the comparison shown here indicates (as did the calculations) that excitation of the projectile without changing its charge is not a major source of stopping-power losses.

Detailed calculations such as those of Dalgarno and Griffing are not available for helium beams in hydrogen gas, and in comparison with our experimental  $\epsilon_0(\text{He}^0)$  and  $\epsilon_1(\text{He}^+)$  we can only show stopping powers calculated as in Tables VII and VIII, which are not strictly comparable to our  $\epsilon_i$  values since they neglect excitation of the electronic structure of the projectile. The measured  $\epsilon_1(\text{He}^+)$  lies below the calculated stopping power for  $\text{He}^+$ , as was the case for protons (see Fig. 6).

The greatest discrepancy is between the measured  $\epsilon_0(\text{He}^0)$  values and the calculated stopping power for a  $\text{He}^0$  projectile. The observed values of  $\epsilon_0(\text{He}^0)$  are about 1.7 times the calculated neutral atom stopping power. The most obvious place to look for the source of the discrepancy is in collisions which excite the electrons in the  $\text{He}^0$  structure without ionizing it, but the evidence from  $\epsilon_0(\text{H}^0)$  indicates that not more than 10% of the stopping losses arise from such collisions, and the high partial atomic stopping power of  $\text{He}^0$  awaits explanation.

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### Fredholm Determinants Applied to Electron-Hydrogen Scattering\*

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The properties of the Fredholm determinant for the electron-hydrogen atom system are discussed. These properties are used to derive formulas for the elastic-scattering phase shifts. *S*- and *P*-wave phase shifts are calculated for low energies and the results are compared with other recent calculations. Exchange effects are fully accounted for in the formalism, and a formula is given for the scattering amplitude when two exit channels are present.

#### I. INTRODUCTION

THE method of Fredholm determinants has been applied to low-energy meson-nucleon scattering by Baker.<sup>1</sup> Because this approach appears to have met with some success, it is interesting to ask whether Fredholm determinants can contribute anything to the theory of low-energy atomic scattering. Several desirable properties of this method suggest that they can.

One such property is the fact that unitarity is satisfied in all orders of approximation whereas the various approximations to the Born series do not satisfy the unitarity condition. Secondly, one obtains expressions for the phase shifts which, in the zero-energy region, are of the form prescribed by effective range theory. At higher energies, presumably the region where the Born series becomes valid, we obtain an expression which approaches the Born series.

In this paper we will treat the elastic scattering of electrons by atomic hydrogen in the energy region from near zero to about eight volts. No effective polarization potential will be included in the Hamiltonian, and the

nucleus will be assumed to be static. The Hamiltonian is expressed in terms of the mass of the electrons and their charge as follows:

$$H = -\frac{1}{2m}\nabla_1^2 - \frac{1}{2m}\nabla_2^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_R. \quad (1)$$

The constant  $E_R$  adjusts the energy levels of the system so that the eigenvalue of  $H$  is zero when the incoming particle has zero energy and the atom is in the ground state.

Although spin does not appear in the Hamiltonian, we will assume that the wave function for the system will include a description of the spin state. Thus, since we are dealing with two identical Fermi-Dirac particles, we will consider only those wave functions which are antisymmetric under simultaneous interchange of both the spatial as well as the spin coordinates.

We will divide the Hamiltonian into an unperturbed part, and an interaction term, denoted by  $H_0$  and  $H_1$ , respectively:

$$H_0 = -\frac{1}{2m}\nabla_1^2 - \frac{1}{2m}\nabla_2^2 - \frac{e^2}{r_2} + E_R, \quad (2)$$

$$H_1 = -\frac{e^2}{r_1} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (3)$$

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<sup>1</sup> M. Baker, *Ann. Phys. (N. Y.)* 4, 271 (1958).

The eigenfunctions of  $H_0$ , normalized to a large spherical box of radius  $R$ , are

$$|klm; n'l'm'\rangle = (2/R)^{1/2} k j_l(kr_1) Y_l^m(\theta_1, \phi_1) \psi_{n'l'm'}(\mathbf{r}_2), \quad (4)$$

where  $\psi_{n'l'm'}(\mathbf{r}_2)$  are the hydrogenic wave functions,  $j_l(kr_1)$  the spherical Bessel functions and  $Y_l^m(\theta_1, \phi_1)$ , the spherical harmonics. By our choice of  $H_0$ , all the eigenvalues are positive. Due to our choice of box normalization they are all discrete and a family of discrete eigenvalues belongs to each state of the hydrogen atom.

$H_0$  is not symmetric under interchange of coordinates of the two electrons so we will not be able to antisymmetrize the eigenfunctions of  $H_0$ . We will, however, require that the eigenfunctions of the total Hamiltonian be antisymmetric. This will be accomplished formally by the antisymmetrization operator  $A$  which, when operating on a two-particle wave function, will result in a wave function which is antisymmetric.  $A$  is a projection operator and therefore has the property

$$A^2 = A. \quad (5)$$

We may decompose  $A$  into one factor which operates on the configuration-space coordinates and another which operates on the spin coordinates. In the subspace of antisymmetric states the following relation holds:

$$A_c S_s + S_c A_s = 1, \quad (6)$$

where the subscripts  $c$  and  $s$  refer to configuration and spin space, respectively, and the operators  $S_{(c,s)}$  and  $A_{(c,s)}$  are the symmetrization and antisymmetrization operators for the corresponding coordinates.

It is clear from Eq. (6) that we require both those eigenfunctions of the total Hamiltonian which are symmetric and antisymmetric under the interchange of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . The symmetries of the wave function outlined above will be used to investigate the properties of the Fredholm determinant. The decomposition of the determinant into subdeterminants allows us to derive the scattering data of the system by use of the relation

$$\Delta E_{\gamma k} = - (1/\pi) \delta_{\gamma k}(E) dE, \quad (7)$$

which occurs in various places in the literature.<sup>1,2</sup>  $\delta_{\gamma,k}(E)$  is the phase shift of the state specified by the eigenvalues  $\gamma$  and  $k$ ,  $\Delta E_{\gamma k}$  is the energy shift between the perturbed and the corresponding unperturbed energy levels, and  $dE$  is the separation of unperturbed levels. The magnitude of the momentum of the incoming particle is taken to be  $k$ , and  $\gamma$  is the remainder of a complete set of commuting observables describing the state of the incoming electron and of the hydrogen atom. Equation (7) does not hold, of course, for bound states.

## II. DECOMPOSITION OF THE FREDHOLM DETERMINANT

We will outline the analysis of the Fredholm determinant, extracting from it whatever is necessary for

<sup>1</sup> B. S. DeWitt, Phys. Rev. **103**, 1565 (1956).

the description of the scattering process. In order to keep to the point of this paper, which is scattering, our outline will be brief. More detail can be found in Ref. 1.

The Fredholm determinant  $D(E)$  is defined by

$$D(E) = \det \left( \frac{E - H}{E - H_0} \right) = \det(1 - G_0(E)H_1), \quad (8)$$

where

$$G_0(E) = (E - H_0)^{-1}. \quad (9)$$

$D(E)$  may also be written in the form

$$D(E) = \prod_{\gamma} \prod_k \left( \frac{E - E_{\gamma k}}{E - E_{0\gamma k}} \right), \quad (10)$$

where  $E_{0\gamma k}$  and  $E_{\gamma k}$  are the eigenvalues of  $H_0$  and  $H$ , respectively.

It is clear from Eq. (10) and the Hermiticity of  $H$  and  $H_0$  that  $D(E)$  has an infinite set of zeros and poles along the positive real axis.

We may use the energy shifts of Eq. (7), defined by

$$\Delta E_{\gamma k} = E_{\gamma k} - E_{0\gamma k}, \quad (11)$$

to express  $D(E)$  as follows:

$$D(E) = \prod_{\gamma} \prod_k \left( 1 - \frac{\Delta E_{\gamma k}}{E - E_{0\gamma k}} \right), \quad (12)$$

and thereby show the connection between the Fredholm determinant and the phase shifts.

Equation (10) indicates that  $D(E)$  may be decomposed into subdeterminants, each referring to a particular value of each of the eigenvalues represented by  $\gamma$ .

$$D(E) = \prod_{\gamma} D_{\gamma}(E). \quad (13)$$

Let  $P_{\gamma}$  be the projection operator that projects an arbitrary state into the state whose eigenvalues are given by  $\gamma$ . We can represent this state by the ket  $|k\gamma\rangle$ .  $P_{\gamma}$  commutes with  $H_0$  and  $H_1$  and obeys the relations

$$\sum_{\gamma} P_{\gamma} = 1, \quad P_{\gamma} P_{\gamma'} = \delta_{\gamma\gamma'} P_{\gamma}. \quad (14)$$

Thus,

$$\begin{aligned} D(E) &= \det(1 - \sum_{\gamma} P_{\gamma} G_0(E) H_1) \\ &= \det \left[ \prod_{\gamma} (1 - P_{\gamma} G_0(E) H_1) \right] \end{aligned} \quad (15)$$

$$= \prod_{\gamma} \det(1 - P_{\gamma} G_0(E) H_1) = \prod_{\gamma} D_{\gamma}(E),$$

and

$$D_{\gamma}(E) = \det(1 - P_{\gamma} G_0(E) H_1). \quad (16)$$

In connection with Eq. (15) it is wise to notice that the unit operator occurring in the second equality is not identical to that in the first. It is more accurate to denote the second unit operator by the notation  $1_{\gamma}$ , where  $1_{\gamma}$  is the unit operator in the subspace projected

by  $P_\gamma$ . The first unit operator is the infinite outer product of the  $1_\gamma$ 's. This inaccuracy in notation seems to be customary in the literature on Fredholm determinants and will not affect our results.

Although the symmetrization and antisymmetrization operators do not commute with  $H_0$  and  $H_1$  separately, we can show that  $D(E)$  may be decomposed further into subdeterminants which refer to the spatially symmetric and antisymmetric state. Using Eq. (6), we have

$$D_\gamma(E) = \det[1 - (A_c S_s + S_c A_s) P_\gamma G_0(E) H_1]. \quad (17)$$

Now,  $P_\gamma$  commutes with the symmetrization and antisymmetrization operators and

$$\begin{aligned} \det(1 - A_c S_s P_\gamma G_0(E) H_1) \det(1 - S_c A_s P_\gamma G_0(E) H_1) \\ = \det[1 - (A_c S_s + S_c A_s) P_\gamma G_0(E) H_1 \\ + A_c S_s P_\gamma G_0(E) H_1 S_c A_s P_\gamma G_0(E) H_1]. \end{aligned}$$

$S_s$  and  $A_s$  commute with  $G_0(E)$  and  $H_1$  since these operators do not contain spin variables, and  $S_s A_s = 0$  so that

$$\begin{aligned} D(E) = \prod_\gamma \det_S(1 - P_\gamma G_0(E) H_1) \det_A(1 - P_\gamma G_0(E) H_1) \\ = \prod_\gamma D_{\gamma S}(E) D_{\gamma A}(E). \quad (18) \end{aligned}$$

The subscripts  $S$  and  $A$  indicate that the determinant is to be evaluated using spatially symmetric or antisymmetric states.

In Eq. (18) we have split  $D(E)$  up into factors each of which have simple poles;  $\gamma$  and  $S, A$  represent a complete set of eigenvalues for our system, excluding the energy, so that those energy levels of  $H_0$  which are degenerate, each belong to a different  $\gamma$ . Thus, we may express these determinants as

$$D_\gamma(E) = 1 + \sum_{E_{0\gamma k}} \frac{r_\gamma(k)}{E - E_{0\gamma k}}, \quad (19)$$

where  $r_\gamma(k)$  are the residues of the simple poles of  $D_\gamma(E)$ . We have suppressed the  $A$  or  $S$  subscripts of the  $D_\gamma(E)$  in Eq. (19) but it must be kept in mind that the spatial symmetry of our system is one of the constants of the motion. The range of the sum in Eq. (19) is essentially determined by  $\gamma$ . For example, if  $\gamma$  specifies the hydrogen atom to be in its ground state, then  $E_{0\gamma k}$  ranges

from zero to infinity. On the other hand, if  $\gamma$  specifies the hydrogen atom to be initially in a  $2s$  state, then  $E_{0\gamma k}$  ranges from  $\frac{3}{4}$  Ry to infinity. Thus, we see that we have yet another degeneracy in  $D_\gamma(E)$ , related to the state of excitation of the atom.

If we have a state with energy less than that required for excitation of the atom from the  $1s$  to, say, the  $2s$  level we will have zero probability of asymptotically finding the atom in the  $2s$  state in the wave function for the system. If we exceed the excitation energy, the asymptotic wave function will contain a linear combination of  $1s$  and  $n=2$ , states and, as the energy is increased beyond higher excitation thresholds, the asymptotic wave function of the system will contain amplitudes for the atom in still higher states. We see, then, that specifying the state of the atom in terms of the principal quantum number  $n$  of a hydrogen atom does not remove the degeneracy of the eigenstates of  $H_0$  which appears for energies of the system which are greater than the energy of the  $n=2$  level.

Nevertheless, we may speak of states for which the atom is predominantly in some level  $n$ . For example, if there are several orthogonal states containing amplitudes for the atom in a  $1s$  state, only one of this number will continuously approach the atomic  $1s$  state as the energy is lowered toward threshold. We will speak of the atom being in a level specified by the quantum number  $n$  but keeping in mind that as the energy of the system is increased beyond an excitation threshold, the resulting degeneracies appearing in the eigenstates of  $H_0$  will have to be removed.

The problem of degeneracy does not appear for energies below the first excitation threshold. In this case we will be dealing with elastic scattering in the strictest sense with a hydrogen atom in its ground state and a free electron in both the incoming and the exit channels. The system will then be described by a set of eigenvalues which we will call  $\gamma_1$  to indicate that the hydrogen atom is in the  $1s$  state. According to Eq. (19) we may write

$$D_{\gamma_1}(E) = 1 + \sum_k \frac{r_{\gamma_1}(k)}{E - E_{0\gamma_1 k}}. \quad (20)$$

Those states which have the same quantum numbers as the set  $\gamma_1$ , except that the atom is in a different energy level, say the  $n$ th, we will denote by the set of eigenvalues  $\gamma_n$ .  $D_\gamma(E)$  may be decomposed as follows:

$$D_\gamma(E) = D_{\gamma_1}(E) \prod_{n=2} D_{\gamma_n}(E), \quad (21)$$

also

$$\begin{aligned} D_\gamma(E) &= \det(1 - G_0(E) H_1 P_\gamma) \\ &= \det\left(1 - G_0^{\neq \gamma_1}(E) H_1 P_\gamma - \frac{1}{E - E_{0\gamma_1 k}} |k\gamma_1\rangle \langle k\gamma_1| H_1 P_\gamma\right) \\ &= \det(1 - G_0^{\neq \gamma_1}(E) H_1 P_\gamma) \det\left(1 - \frac{|k\gamma_1\rangle \langle k\gamma_1| H_1 P_\gamma (1 - G_0^{\neq \gamma_1}(E) H_1 P_\gamma)^{-1}}{E - E_{0\gamma_1 k}}\right), \end{aligned} \quad (22)$$

where

$$G_0^{\neq\gamma_1}(E) = 1/(E-H_0)(1-|k\gamma_1\rangle\langle k\gamma_1|), \quad (23)$$

and

$$P_\gamma = \sum_n P_{\gamma_n}. \quad (24)$$

By use of the Fredholm expansion it is easy to prove that<sup>1</sup>

$$\det 1 - \frac{|k\gamma_1\rangle\langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma)^{-1}}{E-E_{0\gamma_1k}} = 1 - \frac{\langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma)^{-1}|k\gamma_1\rangle}{E-E_{0\gamma_1k}}, \quad (25)$$

so that

$$D_\gamma(E) = D_{\gamma^{\neq\gamma_1}}(E) \left[ 1 - \frac{1}{E-E_{0\gamma_1k}} \langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma)^{-1}|k\gamma_1\rangle \right], \quad (26)$$

where

$$D_{\gamma^{\neq\gamma_1}}(E) = \det(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma). \quad (27)$$

For energies below the lowest excitation threshold we may combine Eqs. (20) and (21) and compare with Eq. (26) near the simple pole at  $E=E_{0\gamma_1k}$ .

$$\left( 1 + \sum_{k'} \frac{r_{\gamma_1}(k')}{E-E_{0\gamma_1k'}} \right) \prod_{n=2} D_{\gamma_n}(E) \Big|_{E \rightarrow E_{0\gamma_1k}} = D_{\gamma^{\neq\gamma_1}}(E_{0\gamma_1k}) \left\{ 1 - \frac{\langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E_{0\gamma_1k})H_1P_\gamma)^{-1}|k\gamma_1\rangle}{E-E_{0\gamma_1k}} - \frac{d}{dE} \langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E_{0\gamma_1k})H_1P_\gamma)^{-1}|k\gamma_1\rangle + O(E-E_{0\gamma_1k}) \right\}, \quad (28)$$

which we can use to solve for  $r_{\gamma_1}(k)$ .

$$r_{\gamma_1}(k) = -Z D_{\gamma_1^{\neq\gamma_1}}(E_{0\gamma_1k}) \langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E_{0\gamma_1k})H_1P_\gamma)^{-1}|k\gamma_1\rangle, \quad (29)$$

where

$$\begin{aligned} Z^{-1} &= [1 - (d/dE) \langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma)^{-1}|k\gamma_1\rangle]_{E=E_{0\gamma_1k}} \\ &= \frac{D_{\gamma^{\neq\gamma_1}}(E_{0\gamma_1k})}{D_{\gamma_1^{\neq\gamma_1}}(E_{0\gamma_1k}) \prod_{n=2} D_{\gamma_n}(E_{0\gamma_1k})}, \end{aligned} \quad (30)$$

and

$$D_{\gamma_1^{\neq\gamma_1}}(E) = 1 + P \sum_{k'} \frac{r_{\gamma_1}(k')}{E-E_{0\gamma_1k'}}. \quad (31)$$

$P$  indicates that the principal value is taken in the sum in Eq. (31). Equations (29)–(31) give us a method of developing  $r_{\gamma_1}(k)$  to arbitrary order in  $H_1$ , and thereby allowing us to calculate  $D_{\gamma_1}$ . These results are valid even above the threshold for excitation. This can be seen by noticing that, for each of the set of levels degenerate with  $E_{0\gamma_1k}$ , we can extract a factor of  $D_\gamma(E)$  as we did in Eq. (26). If we denote the set of degenerate levels with a prime, we can define a new determinant with a simple pole at  $E=E_{0\gamma_1k}$  as follows:

$$D_{\gamma'}(E) = D_\gamma(E) \Big/ \prod_{\gamma' \neq \gamma_1} \left[ 1 - \frac{\langle k\gamma'|H_1P_\gamma(1-G_0^{\neq\gamma'}(E)H_1P_\gamma)^{-1}|k\gamma'\rangle}{E-E_{0\gamma'k}} \right], \quad (32)$$

and

$$D_{\gamma'}(E) = D_{\gamma^{\neq\gamma_1}}(E) [1 - (1/(E-E_{0\gamma_1k})) \langle k\gamma_1|H_1P_\gamma(1-G_0^{\neq\gamma_1}(E)H_1P_\gamma)^{-1}|k\gamma_1\rangle]. \quad (33)$$

Modifying Eq. (21) in a similar way,

$$\begin{aligned} D_{\gamma'}(E) &= D_{\gamma_1}(E) \left\{ \prod_{n=2} D_{\gamma_n}(E) \Big/ \prod_{\gamma' \neq \gamma_1} \left[ 1 - \frac{1}{E-E_{0\gamma'k}} \langle k\gamma'|H_1P_\gamma(1-G_0^{\neq\gamma'}(E)H_1P_\gamma)^{-1}|k\gamma'\rangle \right] \right\} \\ &= D_{\gamma_1}(E) \left[ \prod_{n=2} D_{\gamma_n}(E) \right]'. \end{aligned} \quad (34)$$

We may now proceed to the result of Eq. (29) by using the appropriate primed quantities in Eq. (28) where again we have a simple pole at  $E = E_{0\gamma_1 k}$ .

### III. SCATTERING FORMALISM

In this section we will derive the relationship between the  $S$  matrix for scattering of electrons by atomic hydrogen in the  $1s$  state and the subdeterminant  $D_{\gamma_1}(E)$ . We will not go deeply into the better known properties of  $S$  other than to say that it represents a unitary transformation from those states with asymptotically outgoing waves and those with asymptotically incoming waves.  $S$  is related to the  $T$  matrix in the following way:

$$S = 1 - 2\pi i \delta(E - H_0) T, \quad (35)$$

where  $T$  is given by the formal solution to the Lippmann-Schwinger relation,<sup>3</sup>

$$T = H_1(1 - G_0(E + i\epsilon)H_1)^{-1}. \quad (36)$$

$G_0(E)$  is defined by

$$G_0(E + i\epsilon) = (E - H_0 + i\epsilon)^{-1}. \quad (37)$$

Our decomposition of  $D(E)$  into subdeterminants containing poles of first order requires the use of eigenfunctions of  $H_0$  in the  $\gamma_n$  representation. This representation is obtained from the set of degenerate eigenfunctions of  $H_0$  by a diagonalization of the operator  $H_1(1 - G_0(E)H_1)^{-1}$ . Clearly then, according to Eqs. (35) and (36),  $T$  and  $S$  are also diagonal in this representation.

Consider the expression

$$\begin{aligned} (D_{\gamma_1}(E - i\epsilon)/D_{\gamma_1}(E + i\epsilon)) &= \det\{[1 - G_0(E - i\epsilon)H_1P_\gamma][1 - G_0(E + i\epsilon)H_1P_\gamma]^{-1}\} \\ &= \det_{\gamma_1}\{1 + [G_0(E + i\epsilon) - G_0(E - i\epsilon)] \\ &\quad \times H_1[1 - G_0(E + i\epsilon)H_1]^{-1}\} \quad (38) \\ &= \det_{\gamma_1}\{1 - 2\pi i \delta(E - H_0)H_1[1 - G_0(E + i\epsilon)H_1]^{-1}\}, \end{aligned}$$

where  $\det_{\gamma_1}$  indicates that the determinant is restricted to a set of states defined by  $\gamma_1$ . Now  $S$ , in the diagonal representation, is given by

$$S_{\gamma_n} = \exp(2i\delta_{\gamma_n}), \quad (39)$$

where  $\delta_{\gamma_n}$  is the phase shift. Thus

$$(D_{\gamma_1}(E - i\epsilon)/D_{\gamma_1}(E + i\epsilon)) = S_{\gamma_1} = \exp(2i\delta_{\gamma_1}). \quad (40)$$

Using Eqs. (20) and (40) it is easy to show that

$$\tan\delta_{\gamma_1}(E) = \frac{\pi r_{\gamma_1}(k)}{1 + P \sum_{k'} r_{\gamma_1}(k')(E - E_{0\gamma_1 k'})^{-1}}. \quad (41)$$

Equations (29) and (41) give us a prescription for calculating the phase shift to arbitrary order in  $H_1$ .

In the case of potential scattering it is clear that  $D_{\gamma_1}(E) = D_\gamma(E)$  and according to Eq. (30)  $Z = 1$ . Combining Eqs. (29), (31), and (41) we get the result

$$\tan\delta_\gamma(E) = -\pi \langle k\gamma | H_1 P_\gamma (1 - G_0^{\neq\gamma_1}(E_{0\gamma_1 k}) H_1 P_\gamma)^{-1} | k\gamma \rangle, \quad (42)$$

which agrees with well-known formulas for potential scattering.<sup>1,3</sup> This result suggests that the state vector

$$|\psi_{\gamma_1 k}\rangle = P_\gamma (1 - G_0^{\neq\gamma_1}(E_{\gamma_1 k}) H_1 P_\gamma) | k\gamma_1 \rangle \quad (43)$$

is an eigenfunction of the total Hamiltonian. This is easily verified:

$$\begin{aligned} P_\gamma | k\gamma_1 \rangle &= P_\gamma (1 - G_0^{\neq\gamma_1}(E) H_1 P_\gamma) \\ &\quad \times (1 - G_0^{\neq\gamma_1}(E) H_1 P_\gamma)^{-1} | k\gamma_1 \rangle \\ &= P_\gamma \left[ \left( 1 - \frac{1}{E - E_0} H_1 \right) |\psi_{\gamma_1 k}\rangle \right. \\ &\quad \left. + \frac{P_\gamma}{E - E_{0\gamma_1 k}} | k\gamma_1 \rangle \langle k\gamma_1 | H_1 |\psi_{\gamma_1 k}\rangle \right] \end{aligned}$$

or

$$(E - E_{0\gamma_1 k})^{-1} P_\gamma (E - E_{0\gamma_1 k} - \langle k\gamma_1 | H_1 |\psi_{\gamma_1 k}\rangle) | k\gamma_1 \rangle = P_\gamma (E - H_0)^{-1} (E - H) |\psi_{\gamma_1 k}\rangle. \quad (44)$$

Recalling that  $D_\gamma(E)$  vanishes if  $E$  is equal to an eigenvalue of  $H$  and since  $D_\gamma^{\neq\gamma_1}(E_{\gamma_1 k})$  is not identically zero, Eq. (26) implies

$$E_{\gamma_1 k} - E_{0\gamma_1 k} - \langle k\gamma_1 | H_1 |\psi_{\gamma_1 k}\rangle = 0, \quad (45)$$

which by Eq. (44) yields

$$(E_{\gamma_1 k} - H) |\psi_{\gamma_1 k}\rangle = 0, \quad (46)$$

and

$$\Delta E_{\gamma_1 k} = \langle k\gamma_1 | H_1 |\psi_{\gamma_1 k}\rangle. \quad (47)$$

Now, clearly  $|\psi_{\gamma_1 k}\rangle$  is not normalized and, in fact,

$$\begin{aligned} \langle \psi_{\gamma_1 k} | \psi_{\gamma_1 k} \rangle &= \langle k\gamma_1 | (1 - P_\gamma H_1 G_0^{\neq\gamma_1}(E_{\gamma_1 k}))^{-1} (1 - G_0^{\neq\gamma_1}(E_{\gamma_1 k}) H_1 P_\gamma)^{-1} | k\gamma_1 \rangle \\ &= 1 + \langle k\gamma_1 | (1 - P_\gamma H_1 G_0^{\neq\gamma_1}(E_{\gamma_1 k}))^{-1} P_\gamma H_1 [G_0^{\neq\gamma_1}(E_{\gamma_1 k})]^2 H_1 P_\gamma (1 - G_0^{\neq\gamma_1}(E_{\gamma_1 k}) H_1 P_\gamma)^{-1} | k\gamma_1 \rangle \\ &= 1 - (d/dE) \langle k\gamma_1 | H_1 P_\gamma (1 - G_0^{\neq\gamma_1}(E_{\gamma_1 k}) H_1 P_\gamma)^{-1} | k\gamma_1 \rangle. \end{aligned} \quad (48)$$

The last two equalities may be verified to any order by simply expanding.

In the limit, as the quantization volume increases,

<sup>3</sup> B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).

$dE$ , and therefore  $\Delta E_{\gamma_1 k}$ , vanishes as  $R^{-1}$ . Exceptions occur in the case of bound states. Thus, as  $R^{-1}$  is made to vanish and  $E_{\gamma_1 k} \rightarrow E_{0\gamma_1 k}$ ,

$$\langle \psi_{\gamma_1 k} | \psi_{\gamma_1 k} \rangle \rightarrow Z^{-1}. \quad (49)$$

We see that  $Z$  plays the same role as the state vector renormalization constant of field theory and it represents the probability of finding the unperturbed state  $|k\gamma_1\rangle$  in the fully interacting state vector  $|\psi_{\gamma_1 k}\rangle$ .

There remains the problem of actually obtaining the unperturbed state  $|k\gamma_1\rangle$  when a degeneracy exists. As we have mentioned, this involves a diagonalization of  $T$ . There are well-known methods for doing this to a given order in the perturbation.

As an example, we will consider the case of a twofold degeneracy, such as would occur in the case of an elec-

tron, with angular momentum zero, incident on an atom in the  $1s$  state with sufficient energy to excite the  $2s$  level.<sup>4</sup> Let us denote the unperturbed state with the atom in the ground state by  $|1\rangle$  and let  $|2\rangle$  represent the state with the atom in the  $n=2$  level. To the zero-order approximation, then, the correct normalized wave functions are  $|1'\rangle$ , given by

$$\begin{aligned} |1'\rangle &= C_{11}|1\rangle + C_{21}|2\rangle, \\ |2'\rangle &= C_{12}|1\rangle + C_{22}|2\rangle, \end{aligned} \quad (50)$$

with

$$\begin{aligned} C_{11} &= \left[ \frac{\langle 1|H_1|2\rangle}{2|\langle 1|H_1|2\rangle|} \left(1 + \frac{\alpha}{\beta}\right) \right]^{1/2}, & C_{21} &= \left[ \frac{\langle 2|H_1|1\rangle}{2|\langle 1|H_1|2\rangle|} \left(1 - \frac{\alpha}{\beta}\right) \right]^{1/2}, \\ C_{12} &= \left[ \frac{\langle 1|H_1|2\rangle}{2|\langle 1|H_1|2\rangle|} \left(1 - \frac{\alpha}{\beta}\right) \right]^{1/2}, & C_{22} &= - \left[ \frac{\langle 2|H_1|1\rangle}{2|\langle 1|H_1|2\rangle|} \left(1 + \frac{\alpha}{\beta}\right) \right]^{1/2}, \end{aligned} \quad (51)$$

where

$$\alpha = \langle 1|H_1|1\rangle - \langle 2|H_1|2\rangle, \beta = (\alpha^2 + 4|\langle 1|H_1|2\rangle|^2)^{1/2}. \quad (52)$$

As the energy of the incoming electron is reduced below threshold the degeneracy of states no longer occurs. This obviates the necessity of diagonalizing  $H_1$  and  $|1'\rangle = |1\rangle$ , and  $|2'\rangle = |2\rangle$ .

The matrix  $C = [C_{ij}]$  gives us a transformation which diagonalizes  $T$  in first order. The procedure we propose for calculating the transition amplitude  $T_{21}$  is to calculate the  $T$  matrix in diagonal form, which we will denote by  $T'$ , and then use the inverse transformation to get the off-diagonal elements.  $T'$  can be calculated by using

Eqs. (35), (40), and (41):

$$T'_i(E) = \frac{r_i(k)}{1 + \sum_{k'} r_i(k')(E - E_{k'} + i\epsilon)^{-1}}, \quad (53)$$

and  $T_{12}(E)$  is given to lowest order by

$$T_{12}(E) = (CTC^\dagger)_{12} = C_{21}C_{11}^*T'_1(E) + C_{22}C_{12}^*T'_2(E). \quad (54)$$

From Eqs. (51) we see that

$$C_{21}C_{11}^* = -C_{22}C_{12}^* = \langle 2|H_1|1\rangle/\beta, \quad (55)$$

and

$$\begin{aligned} r_1(k) &= \frac{1}{2}(\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle + \beta) = \langle 1|H_1|1'\rangle, \\ r_2(k) &= \frac{1}{2}(\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle - \beta) = \langle 2|H_1|2'\rangle, \end{aligned} \quad (56)$$

which, when combined with Eqs. (53) and (54), yields the following amplitude for excitation:

$$T_{21} = \frac{\langle 2|H_1|1\rangle}{2\beta} \left\{ \frac{\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle + \beta}{1 + \frac{1}{2} \sum_{k'} [\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle + \beta](E - E_{k'} + i\epsilon)^{-1}} - \frac{\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle - \beta}{1 + \frac{1}{2} \sum_{k'} [\langle 1|H_1|1\rangle + \langle 2|H_1|2\rangle - \beta](E - E_{k'} + i\epsilon)^{-1}} \right\}. \quad (53a)$$

#### IV. CALCULATION OF ELASTIC S- AND P-WAVE SCATTERING

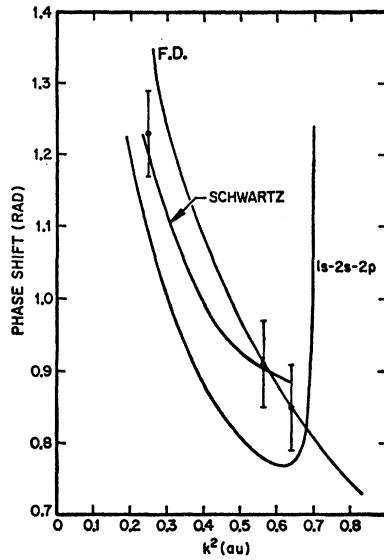
The theory of scattering, as presented in the previous section, will now be applied to the scattering of electrons by atomic hydrogen. We present only the lowest order approximation for  $S$ - and  $P$ -wave scattering using the interaction term of Eq. (3) and the wave functions of Eq. (4). Our basic approximation consists of using

the lowest order term of Eq. (29) for the residues:

$$r_{\gamma_1}(k) = -\langle \gamma_1|H_1 P_\gamma|\gamma_1\rangle. \quad (29a)$$

<sup>4</sup>In fact there is a fivefold degeneracy in the scattering states but we have used a quadratic secular equation because it is easier to handle and serves the purpose of illustration. This assumption is in the spirit of the so-called strong-coupling approximation which assumes that the  $1s-1s$ ,  $1s-2s$ , and  $2s-2s$  transition amplitudes are coupled together.

FIG. 1. Singlet  $S$  phase shifts as a function of  $k^2$ . F. D. refers to the Fredholm determinant calculation. Various other calculations are included for comparison. The three bracketed points are the results of Temkin (Ref. 7).



All the results are obtained in closed form and involve no machine calculations. For  $S$ -wave scattering the results are

$$r_{0s}(k) = \frac{1}{4\pi} \left\{ \frac{k(13 - 2k^2 + k^4)}{(1 + k^2)^3} + \frac{1}{k} \ln(1 + k^2) \right\}, \quad (57)$$

$$r_{0t}(k) = \frac{1}{4\pi} \left\{ \frac{k(-11 + 6k^2 + k^4)}{(1 + k^2)^3} + \frac{1}{k} \ln(1 + k^2) \right\};$$

$$P \int_0^\infty \frac{r_{0s}(k') dE'}{E - E'} = \frac{1}{2} \left\{ \frac{1}{k} \tan^{-1} k - \frac{5 - 10k^2 + k^4}{2(1 + k^2)^3} \right\}, \quad (58)$$

$$P \int_0^\infty \frac{r_{0t}(k') dE'}{E - E'} = \frac{1}{2} \left\{ \frac{1}{k} \tan^{-1} k - \frac{-3 + 14k^2 + k^4}{2(1 + k^2)^3} \right\}.$$

The subscript 0 refers to the orbital angular momentum of the scattered electron and  $s$  and  $t$  refer to the singlet and triplet scattering states, respectively;  $k$  is the momentum of the scattered particle in units of  $me^2$  so that  $k=1$  corresponds to an energy of 1 Ry for the incoming particle.

FIG. 2. Triplet  $S$  phase shifts as a function of  $k^2$ .

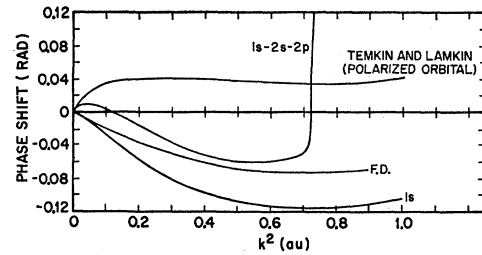
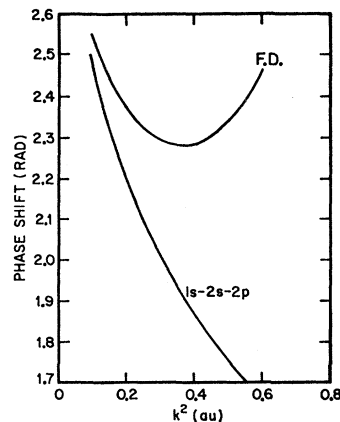


FIG. 3. Singlet  $P$  phase shifts as a function of  $k^2$ .

Taking the limit of Eqs. (57) and (58), as  $k$  approaches zero, and using the result in Eq. (41), we get the following zero-energy forms for the phase shifts:

$$\begin{aligned} k \cot \delta_{0s} &= - (3/14) + \frac{1}{2} (73/21) k^2, \\ k \cot \delta_{0t} &= - \frac{1}{2} + \frac{1}{2} (67/15) k^2. \end{aligned} \quad (59)$$

The form of Eqs. (59) agrees with effective range theory and they have reasonable values for the effective ranges and scattering lengths. The present calculation is compared with other recent calculations in Table I.

TABLE I. Zero-energy scattering data.

	Other calculations	Present calculation
Singlet effective range	3.20 <sup>a</sup>	3.48
scattering length	6.2 <sup>b</sup>	4.66
Triplet effective range	4.4-4.8 <sup>a</sup>	4.46
scattering length	1.98 <sup>a</sup>	2.00

<sup>a</sup> Close-coupling calculation by Burke and Schey (Ref. 5).  
<sup>b</sup> Upper limit calculated by variational method [L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. 119, 164 (1960)].

The scattering data we use for comparison are selected from the review article by Burke and Smith.<sup>5</sup> The triplet scattering length used as a comparison is more to be considered as an upper limit.

The singlet and triplet phase shifts are displayed in Figs. 1 and 2, and the results are compared with the calculations of Burke and Schey,<sup>6</sup> Temkin,<sup>7</sup> and Schwartz.<sup>8</sup> In Fig. 2, only the close-coupling calcula-

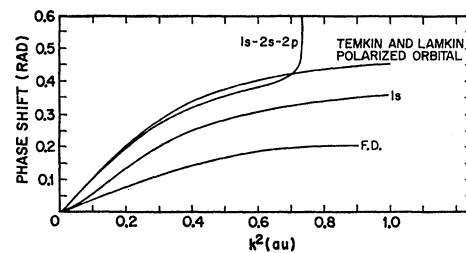


FIG. 4. Triplet  $P$  phase shifts as a function of  $k^2$ .

<sup>5</sup> P. G. Burke and K. Smith, Rev. Mod. Phys. 34, 458 (1962).

<sup>6</sup> P. G. Burke and H. M. Schey, Phys. Rev. 126, 147 (1962).

<sup>7</sup> A. Temkin, Phys. Rev. 126, 130 (1962).

<sup>8</sup> C. Schwartz, Phys. Rev. 124, 1468 (1961).

tion<sup>6</sup> is used as a comparison because the results of the other authors lie very close to it. As the energy increases, the agreement gets progressively worse for the

triplet-state scattering until at  $k^2=0.6$  ( $E \approx 8$  V) the discrepancy in the phase shifts is about 50%.

The  $P$ -wave results are

$$\begin{aligned} \pi r_{1s}(k) &= \left[ \frac{1}{4k} - \frac{2(1+6k^2-3k^4)}{3k^3(1+k^2)^3} \right] \ln(1+k^2) + \frac{32}{3(1+k^2)^3} \tan^{-1}k - \frac{k}{4(1+k^2)} + \frac{2-21k^2-3k^4}{3k(1+k^2)^3}, \\ \pi r_{1t}(k) &= \left[ \frac{1}{4k} + \frac{2(1+6k^2-3k^4)}{3k^3(1+k^2)^3} \right] \ln(1+k^2) - \frac{32}{3(1+k^2)^3} \tan^{-1}k - \frac{k}{4(1+k^2)} - \frac{2-21k^2-3k^4}{3k(1+k^2)^3}, \end{aligned} \quad (60)$$

$$\begin{aligned} P \int_0^\infty \frac{r_{1s}(k') dE'}{E-E'} &= \left[ \frac{-1}{2k} + \frac{4(1+6k^2-3k^4)}{3k^3(1+k^2)^3} \right] \tan^{-1}k + \frac{16}{3(1+k^2)^3} \ln(1+k^2) \\ &\quad - \frac{64}{3(1+k^2)^3} \ln 2 + \frac{1}{2(1+k^2)} - \frac{4-22k^2-5k^4+6k^6}{3k^2(1+k^2)^3}, \end{aligned} \quad (61a)$$

$$\begin{aligned} P \int_0^\infty \frac{r_{1t}(k') dE'}{E-E'} &= \left[ \frac{-1}{2k} - \frac{4(1+6k^2-3k^4)}{3k^3(1+k^2)^3} \right] \tan^{-1}k - \frac{16}{3(1+k^2)^3} \ln(1+k^2) \\ &\quad + \frac{64}{3(1+k^2)^3} \ln 2 + \frac{1}{2(1+k^2)} + \frac{4-22k^2-5k^4+6k^6}{3k^2(1+k^2)^3}. \end{aligned} \quad (61b)$$

Although these expressions are a bit unwieldy, they demonstrate that the method presented in this paper can be used to get results for low-energy electron-hydrogen atom scattering data in closed form.

The  $P$ -wave results are displayed in Figs. 3 and 4. The agreement for singlet scattering again is good. As was the case for  $S$  waves, the triplet results are somewhat at variance with the other calculations. The present calculation is compared with the  $1s$  and  $1s-2s-2p$  close-coupling calculation<sup>6</sup> as well as the polarized orbital calculation of Temkin and Lamkin.<sup>9</sup> The comparison suggests that the more the effect of polarization is included in the calculation the higher it raises the phase-shift curves. In the Fredholm determinant calculation, polarization effects will show up in higher order approximations by including an atomic  $p$  state as an intermediate state. On this basis it is not unreasonable to expect that by making higher approximations to the residues we will obtain better agreement for the triplet  $P$ -wave phase shifts.

## V. CONCLUSION

Briefly outlined, the prescription for calculating the scattering given in this paper requires a set of eigenfunctions of the unperturbed Hamiltonian which allows a decomposition of the Fredholm determinant into products of subdeterminants having simple poles in the complex energy plane. This set of eigenfunctions is also the set which diagonalizes the  $S$  matrix. We use these eigenfunctions to calculate the residues of the Fred-

holm subdeterminants. The residues are related in a simple way to the phase shifts.

The lack of accurate low-energy experimental data for electron-hydrogen atom scattering requires one to hedge any conclusions regarding the accuracy of a particular calculation. Nevertheless, it does seem clear, when comparing our results with other calculations, that the method of Fredholm determinants offers a useful method of obtaining low-energy data for atomic scattering problems. This seems to be particularly emphasized by the fact that the results of the present calculation were obtained by an approximation simple enough to allow us to do our calculation in closed form. In spite of the simplicity of our calculation the results compare favorably with calculations using rather complicated solutions to the Schrödinger equation which can only be solved by machine computation. Further work is under way for the electron-hydrogen system which will include an attempt to carry the  $S$ - and  $P$ -wave calculations to higher order and to determine the  $1s-2s$  inelastic scattering amplitude as outlined in Sec. III. We expect to carry out these computations using a machine program rather than finding the matrix elements analytically as we did in this paper.

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<sup>9</sup> A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).