Singlet e-H scattering at intermediate energies*

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(Received 17 December 1973)

Using Fredholm techniques employing only square-integrable basis functions, elastic s- and p-wave singlet electron–hydrogen–atom cross sections are calculated for the energy range 10–27 eV, that is, at energies where a continuum of open channels is present. The s and p amplitudes are combined with higher partial-wave amplitudes taken from earlier close-coupling results, to give singlet e-H elastic angular distributions at and above the ionization threshold.

I. INTRODUCTION

At incident energies above 0.5 hartrees, electrons colliding with ground-state hydrogen atoms can ionize the target, implying the existence of an infinite number of final-state channels which must be taken into account even for the calculation of the elastic cross section. In any practical calculation, this infinite number of degrees of freedom must be reduced to a finite number; the Fredholm-optical-potential technique introduced here represents one approach to this reduction. Qualitatively, earlier Fredholm calculations using square-integrable (L^2) basis sets have implied that a branch cut corresponding to a single open channel may be conveniently represented by a small number of discrete poles, which arise from the discretization of the unperturbed-channel Hamiltonian in the L^2 basis set. The present development suggests a natural extension of this idea; that is, a multiparticle ionization cut may be represented by the poles (and residues) generated by the appropriate L^2 configuration interaction for the multiparticle system.

The plan of the paper is as follows: The calculation of substituted Fredholm determinants via the method of complex basis functions, and the construction of the elastic scattering amplitude are reviewed in Sec. II A. In Sec. II B the construction of an inelastic optical potential which takes particle indistinguishability into account properly is discussed. Section III contains the results of application of these techniques to the problem of elastic singlet e-H scattering; s- and p-wave cross sections are presented and compared with results obtained using close-coupling techniques[1-4] and T-matrix extrapolation[5] methods. Composite Fredholm close-coupling angular distributions including partial waves with $l = 0, 1, \ldots, 5$ are presented. A summary and discussion are contained in Sec. IV.

II. THEORETICAL BACKGROUND

A. L^2 Fredholm calculations of scattering amplitude

Earlier[6-8] work has shown that approximations to the single-channel partial-wave Fredholm determinant $D(z) = \det[(z - H)/(z - H^0)]$ may be obtained from the matrix representations $\bar{H}$ and $\bar{H}^0$ of the scattering Hamiltonian and kinetic energy, taken in an L^2 basis. The approximate determinant

$$D^{\text{approx}}(z) = \det\left(\frac{z - \bar{H}}{z - \bar{H}^0}\right) = \prod_i \left(\frac{z - E_i}{z - E_i^0}\right) \qquad (2.1)$$

—where E_i^0 and E_i are the eigenvalues of $\bar{H}^0$ and $\bar{H}$, respectively—can approximate $D(z)$ for complex z, away from the elastic cut; scattering phase shifts may be obtained by calculating the appropriate $z \to E + i\epsilon$ limit.[9] This limit may be taken using rational-fraction analytic continuation,[6,7] equivalent quadrature,[10] or Stieltjes imaging[11] techniques, and yields an approximate phase shift through the well-known relationship[9,12]

$$D(E + i\epsilon) = |D(E + i\epsilon)| e^{-i\delta(E)}. \qquad (2.2)$$

Calculation of inelastic-scattering amplitudes or even the elastic amplitude at energies where more than one channel is open requires knowledge of the substituted Fredholm determinants.[13] The elastic S-matrix element is given by[13,14]

$$S_{1s1s}(E) = D_{1s}(E + i\epsilon)/D(E + i\epsilon), \qquad (2.3)$$

where D_{1s} is the "substituted" Fredholm determinant. The substituted determinants may be regarded as arising from taking the $z \to E + i\epsilon$ limit of the multichannel Fredholm determinant starting on appropriate nonphysical Reimann sheets.[14,15] For the calculation of elastic e-H amplitudes, the appropriate limits are shown in Fig. 1: Continuation path a may be used to take the $E + i\epsilon$ above all of the cuts and yields $D(E + i\epsilon)$; path b starts "below" the elastic 1s cut and takes the $E + i\epsilon$

limit with respect to all other cuts. The method of complex L^2 basis functions[15] which allows the "rotation" of the elastic cut—giving the determinants $D^\theta(z)$ and $D^{\theta*}(z)$, respectively, as shown in Fig. 1, and thus allowing calculation of the appropriate substituted determinants—is fully discussed in Ref. 15, where a technique of calculation of inelastic scattering amplitudes using L^2 basis sets is developed.

B. Construction of an inelastic optical potential

For electron–hydrogen-atom scattering, a natural decomposition of the Hamiltonian into H and H^0 is[7]

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + 1/r_{12}, \qquad (2.4a)$$

$$H^0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1, \qquad (2.4b)$$

$$V = -1/r_2 + 1/r_{12}, \qquad (2.4c)$$

which, appropriately, leads to a Fredholm determinant $D(z) = \det[(z - H)/(z - H^0)]$, with an elastic branch cut beginning at -0.5 a.u. Since the

decomposition of Eq. (2.4) is not symmetric with respect to particle interchange, problems that are not present when considering only elastic e-H scattering arise when an attempt is made to extract scattering information at energies above the first inelastic threshold. For example, if the configuration $|1s2s|$ is included in the basis used to diagonalize H, then are we to include $1s(1)2s(2)$ or $1s(2)2s(1)$ in the L^2 set used to diagonalize H^0? If we use both, $\bar{H}$ and $\bar{H}^0$ have different dimensionalities, giving $D^{\mathrm{approx}}(z)$ incorrect asymptotic behavior as a function of z; if we are to keep only one, the definition of $\bar{H}^0$ becomes arbitrary, and a unique phase, or set of substituted determinants, cannot be extracted. This problem of the differing permutation symmetries of H and H^0 is more fully discussed in Ref. 8, where it is shown that a simple solution to the above-mentioned ambiguity is to use an optical potential.

Defining a projector[16] P to project onto the elastic channel, and Q to be its orthogonal complement, we have

$$D(z) = \det\left(\frac{z - H}{z - H^0}\right) = \det\begin{pmatrix} z - H_{PP} & -H_{PQ} \\ -H_{QP} & z - H_{QQ} \end{pmatrix} \Big/ \det\begin{pmatrix} z - H_{PP}^0 & 0 \\ 0 & z - H_{QQ}^0 \end{pmatrix}$$

$$= \det\left(\frac{z - H_{QQ}}{z - H_{QQ}^0}\right) \det\left\{ \left[z - H_{PP} - H_{PQ}\left(\frac{1}{z - H_{QQ}}\right) H_{QP} \right] \Big/ (z - H_{PP}^0) \right\}. \qquad (2.5)$$

The elastic S-matrix element is given by

$$\frac{D_{1s}(E + i\epsilon)}{D(E + i\epsilon)} = \frac{\det\left[(E + i\epsilon - H_{QQ})/(E + i\epsilon - H_{QQ}^0)\right] \det\left\{[E - i\epsilon - H_{PP} - H_{PQ}(E + i\epsilon - H_{QQ})^{-1}H_{QP}]/(E - i\epsilon - H_{PP}^0)\right\}}{\det\left[(E + i\epsilon - H_{QQ})/(E + i\epsilon - H_{QQ}^0)\right]\det\left\{[E + i\epsilon - H_{PP} - H_{PQ}(E + i\epsilon - H_{QQ})^{-1}H_{QP}]/(E + i\epsilon - H_{PP}^0)\right\}}$$

$$= \frac{D_{1s}^{\mathrm{opt}}(E + i\epsilon)}{D^{\mathrm{opt}}(E + i\epsilon)}, \qquad (2.6)$$

where

$$D^{\mathrm{opt}}(E + i\epsilon) = \det\left\{[E + i\epsilon - H_{PP} - H_{PQ}(E + i\epsilon - H_{QQ})^{-1}H_{QP}]/(E + i\epsilon - H_{PS}^0)\right\}, \qquad (2.7a)$$

$$D_{1s}^{\mathrm{opt}}(E + i\epsilon) = \det\left\{[E - i\epsilon - H_{PP} - H_{PQ}(E + i\epsilon - H_{QQ})^{-1}H_{QP}]/(E - i\epsilon - H_{PP}^0)\right\}, \qquad (2.7b)$$

the factor $\det[(z - H_{QQ})/(z - H_{QQ}^0)]$ canceling identically.

The projected operators H_{PP}^0 and H_{PP} most appropriate for use in the present L^2-Fredholm calculations are explicitly defined by their matrix representations:

$$(\bar{H}_{PP}^0)_{ij} = \int d^3r_1\, d^3r_2\, \phi_{1s}(r_1)\chi_i(r_2)$$

$$\times H^0(r_1r_2)\phi_{1s}(r_1)\chi_j(r_2), \qquad (2.8a)$$

where the $\chi_i(r_2)$ are members of an orthonormal

complete discrete L^2 basis $\{\chi_i(r)\}$. $\bar{H}_{PP}$ is defined in terms of the normalized and antisymmetrized versions of the functions $\phi_{1s}(r_1)\chi_i(r_2)$; thus

$$(\bar{H}_{PP})_{ij} = \int d^3r_1\, d^3r_2\, \phi_{1s}(r_1)\chi_i(r_2)$$

$$\times H(r_1r_2)\phi_{1s}(r_1)\chi_j(r_2)$$

$$\pm \int d^3r_1\, d^3r_2\, \phi_{1s}(r_1)\chi_i(r_2)$$

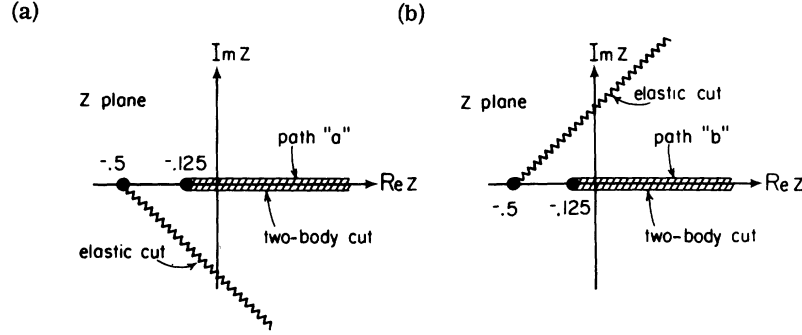$$\times H(r_1r_2)\chi_j(r_1)\phi_{1s}(r_2), \qquad (2.8b)$$

(a)　　　　　　　　　　　　　　(b)

FIG. 1. Branch-cut structure of $D^\theta(z)$, $D^{\theta*}(z)$ Fredholm determinants for e-H scattering; the elastic cut has been rotated (Ref. 15) off the real axis via use of complex basis functions. Part (a), showing the cut structure of $D^\theta(z)$, path "a" shows a continuation, which takes the $E + i\epsilon$ limit for all cuts, yielding $D(E + i\epsilon)$. In part (b), which shows the cut structure of $D^{\theta*}(z)$, path "b", which starts "below" the elastic cut (i.e., on the second Reimann sheet), shows a continuation which results in performing the $E - i\epsilon$ limit with respect to the elastic cut, and the $E + i\epsilon$ limit with respect to all other channels, resulting in $D_{1s}(E + i\epsilon)$, the substituted determinant needed for construction of the elastic amplitude. The determinants $D^{\text{opt}(\theta)}(z)$ and $D^{\text{opt}(\theta*)}(z)$ have similar branch structures, and paths "a" and "b" yield $D^{\text{opt}}(E + i\epsilon)$ and $D_{1s}^{\text{opt}}(E + i\epsilon)$, respectively.

with the + for singlets and − for triplets. In terms of $\overline{H}_{PP}^0$ and $\overline{H}_{PP}$, approximations to the "static-exchange" elastic phase shift are constructed by calculating the phase (in the $E + i\epsilon$ limit) of the approximate determinant[7]:

$$D^{\text{SE}}(z) = \det[(z\overline{I} - z\overline{\Delta} - \overline{H}_{PP})/(z\overline{I} - \overline{H}_{PP}^0)], \quad (2.9)$$

where $\overline{H}_{PP}$ and $\overline{H}_{PP}^0$ are given by Eqs. (2.8a) and (2.8b) and the overlap orthogonality term $\overline{\Delta}$ is given by

$$(\overline{\Delta})_{ij} = \int d^3r \phi_{1s}(r)\chi_i(r) \int d^3r \phi_{1s}(r)\chi_j(r); \quad (2.10)$$

$\overline{\Delta}$ arises from taking matrix elements of the unit operator with respect to the antisymmetric (real) wave functions:

$$(1/\sqrt{2})[\phi_{1s}(r_1)\chi_i(r_2) \pm \phi_{1s}(r_2)\chi_i(r_1)]; \quad (2.11)$$

$\overline{\Delta}$ corresponds to the usual orthogonality terms arising in the close-coupling method.

$\overline{H}_{QQ}$ is constructed as per the work of O'Malley and Geltman.[17] That is, each member of a complete discrete one-electron set $\{\phi_i(r)\}$ [not necessarily the same set as the $\{\chi_i(r)\}$ used to solve the static-exchange part of the problem] is orthogonalized to the target ground-state function $\phi_{1s}(r)$, yielding a new set $\{\overline{\phi}_i(r)\}$ which may be assumed, without loss of generality, to have been reorthogonalized and normalized. $\overline{H}_{QQ}$ is then constructed by calculating matrix elements of H with respect to the properly symmetrized two-electron functions

$$(1/\sqrt{2})[\overline{\phi}_i(r_1)\overline{\phi}_j(r_2) \pm \overline{\phi}_j(r_1)\overline{\phi}_i(r_2)]. \quad (2.12)$$

The operators H_{PP}^0, H_{PP}, and H_{QQ} are now com-

pletely defined in Hilbert space by their matrix representations. The fact that the projector P, when applied to H^0, excludes all configurations where the "target" electron is excited (electron 1 in our notation) makes the definition of $\overline{H}_{PP}^0$ unambiguous once the single-particle basis has been specified.[8] The ambiguous parts of $\overline{H}^0$ are now all contained in $\overline{H}_{QQ}^0$, whose explicit construction is avoided in this optical potential formulation.

III. CALCULATIONS AND RESULTS

Using the method of complex basis functions,[15] in conjunction with the inelastic optical potential discussed in Sec. II B, the determinants D^{opt} and D_{1s}^{opt} were approximated. Specifically, $\overline{H}_{PP}^0$ was constructed using configurations of the form $\phi_{1s}(r_1)\chi_i(r_2 e^{\pm i\phi})$, and $\overline{H}_{PP}$ was constructed from the symmetrized configurations

$$\phi_{1s}(r_1)\chi_i(r_2 e^{\pm i\phi}) + \phi_{1s}(r_2)\chi_i(r_1 e^{\pm i\phi}),$$

the $\pm$ determining whether the elastic cut is rotated "up" or "down" by 2ϕ in the complex z plane.[15] $\overline{H}_{QQ}$ was formed by computing the matrix representation of H_{QQ} using two-electron configurations formed from (real) one-electron functions, orthogonalized to ϕ_{1s}.

The potential

$$V^{\text{opt}}(z) = H_{PQ}\left(\frac{1}{z - H_{QQ}}\right)H_{QP},$$

has a "two-body" cut, corresponding to the spectrum of the operator H_{QQ}, which remains on the real axis. The cut structure of D^{opt} and D_{1s}^{opt} is thus that of Figs. 1(a) and 1(b), respectively, D^{opt} being calculated with the transformation $r_2 \rightarrow r_2 e^{+i\phi}$

and D_{1s}^{opt} with the transformation $r_2 \to r_2 e^{-i\phi}$. In actual calculations, the rotated elastic cut is replaced by a row of poles corresponding to the (complex) eigenvalues of $\bar{H}_{PP}^0$, and the two-body cut replaced by a row of poles corresponding to the (real) eigenvalues of $\bar{H}_{QQ}$. The eigenvalues of $\bar{H}_{PP}^0$ are simply given by $E_i = -\frac{1}{2} + E_i^{KE}$, where the eigenvalues E_i^{KE}, which are the eigenvalues of the matrix representation of kinetic energy, are either known analytically[10] or easily found if a Laguerre-type basis is used for the diagonalization. More importantly, the pole distribution generated by use of a Laguerre basis in the construction of $\bar{H}_{PP}^0$ forms a set of abscissas corresponding to a Gaussian-equivalent quadrature with known weights,[18,19] allowing the embedding of the discrete representation of the elastic cut into an appropriate approximation to the actual cut via the dispersion-correction technique of Refs. 10 and 20. This embedding allows the use of small rotations for the calculation of D_{1s}^{opt}.[15,21] Rational-fraction continuation is used to take the $E + i\epsilon$ limit on the upper lip of the two-body cut defined by the optical potential. $V^{opt}(z)$ is, of course, complex in the $E + i\epsilon$ limit, the imaginary part being due to flux leaving the elastic channel into all channels open at a given energy, including ionization channels. We note that rational-fraction continuation is necessitated by the pole approximation to the inelastic optical potential, not by the discrete approximation to $(E - \bar{H}_{PP}^0)^{-1}$, whose analytic structure is correctly handled by dispersion correction.[10,20]

A. Singlet s-wave cross section

1. Purely elastic scattering

To test the complex coordinate technique and the construction of the optical potential, purely elastic singlet s-wave phase shifts were calculated

TABLE I. Static-exchange singlet s-wave electron-hydrogen phase shifts (rad) computed using a basis of Slater-type radial functions, with and without complex basis functions. A small but systematic error is introduced by the use of complex basis functions (see Refs. 15 and 21).

k (a.u.)	δ_0^+ (No rotation)[a]	δ_0^+ ($\phi = 0.1$ rad)[b]	δ_0^+ ("exact")
0.2	1.871	1.862	1.870
0.4	1.241	1.232	1.239
0.6	0.871	0.862	0.869
0.8	0.653	0.645	0.651

[a] Calculations performed with the free electron described by the 14 Slater functions $r_2^n e^{-\xi_s r_2}$, where $n = 0, 2, \ldots, 13$ and $\xi_s = 1.0$.

[b] For these calculations, the Slater-function coordinates (see Ref. a) were "rotated" by 0.1 rad, i.e., $r_2 \to r_2 e^{-i(0.1)}$.

for the electron–hydrogen-atom problem. For solution of the e-H problem in the static-exchange approximation, H_{PP}^0 was diagonalized in the basis $\phi_{1s}(r_1)\chi_i(r_2)$, where the $\chi_i(r_2)$ were chosen to be the 14 Slater functions $r_2^n e^{-\xi_s r_2}$, $n = 0, \ldots, 13$, with $\xi_s = 1.0$, with appropriate angular factors. The set generated a Chebyschev-type equivalent quadrature.[10,18] H_{PP} (the static-exchange Hamiltonian) was diagonalized in the same basis, appropriately symmetrized.[7] Results for the singlet s-wave static-exchange phase shift with and without the transformation $r_2 \to r_2 e^{i\phi}$ are given in Table I; as expected,[21] coordinate rotation introduced a small error in the calculated phase shifts.[22] Correlated singlet s-wave e-H results obtained by construction of $V^{opt}(z)$ formed by diagonalizing H_{QQ} in the basis of all configurations generated from eight s-type orbitals and five p-type orbitals, using $\bar{H}_{PP}^0$ and $\bar{H}_{PP}$ from the static-exchange calculation, are shown in Table II, where they are compared with an earlier s-p limit calculation; again, coordinate rotation introduces a small but systematic error.

2. s-wave elastic scattering at intermediate energies

The radial-limit singlet s-wave cross section was calculated using the static-exchange basis of Sec. III A 1 to construct $\bar{H}_{PP}^0$ and $\bar{H}_{PP}$; the s-type radial Slater functions $r^n e^{-\xi_s r}$, with $n = 0, \ldots, 7$, and orthogonalized to $\phi_{1s}(r)$, were used to construct $\bar{H}_{QQ}$ [by performing a full configuration interaction (CI) in the basis]. Coordinate rotation and rational-fraction analytic continuation were used to construct the appropriate substituted Fredholm determinants. Figure 2 compares the radial-limit ($\xi_s = 1.0$) results obtained by this method with the radial-limit results of Burke and Mitchell[2] ob-

TABLE II. Correlated singlet s-wave electron-hydrogen elastic phase shifts (rad) computed in the formulation of Sec. II; results are given with and without "rotation" of the elastic cut.

k (a.u.)	δ_0^+ (No rotation)[a]	δ_0^+ ($= 0.1$ rad)	δ_0^+ ("exact")[b]
0.2	2.053	2.043	2.054
0.4	1.401	1.392	1.403
0.6	1.026	1.017	1.029
0.8	0.881	0.865	0.875

[a] Eight s functions and five p functions were used for construction of the optical potential. The s orbitals, $r^n e^{-\xi_s r}$, had exponents of 1.0, 2.5, 2.5, 1.8, 1.2, 0.75, 0.40, and 0.15 (n values were 0 for the first two orbitals and 1 for the others). The p functions were of the form $r e^{-\xi_p r}$, were exponents of 1.0, 0.75, 0.5, 0.3, and 0.15.

[b] Results of an s-p limit calculation by S. A. Adelman and W. P. Reinhardt, Phys. Rev. A $\underline{6}$, 255 (1972).
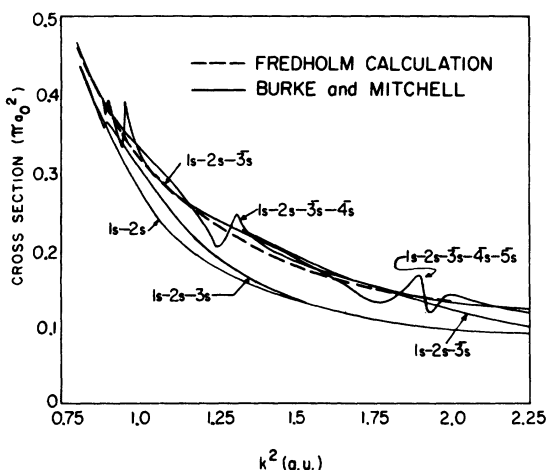
FIG. 2. Singlet s-wave e-H elastic cross section computed in the radial limit (i.e., $\bar{H}_{QQ}$ is diagonalized using configurations formed only from states of s-orbital symmetry) as computed by the Fredholm technique of Sec. III. These results are compared with radial-limit pseudostate close-coupling calculations of Burke and Mitchell (Ref. 2). It is evident that the close-coupling and Fredholm results would be very similar if an appropriate averaging technique were used to eliminate the spurious "pseudothresholds" in the close-coupling calculation. (Statistical factor of $\frac{1}{4}$ is included in this cross section.)

tained using a pseudostate close-coupling technique. Table III gives more detailed radial-limit results, and gives some indication of the stability of the results with respect to changes in the nonlinear parameter ξ_s. Good quantitative agreement with the pseudostate close-coupling results of Burke and Mitchell[2] and Heller and Yamani[4] is obtained, except near the "pseudoresonances" occurring when the close-coupling "pseudochannels" in the ionization region become energetically open.

To obtain fully correlated singlet s-wave cross sections and the s-wave total inelasticity in the ionization region, full configuration interactions were carried out for $\bar{H}_{QQ}$ using all ^1S configurations constructed from eight s-type, eight p-type, and eight d-type basis functions, properly orthogonalized to $\phi_{1s}(r_1)$. The radial s-type functions were taken to be of the form $r^n e^{-\xi_s r}$ ($n = 0, \ldots, 7$); the radial p-type functions were $r^n e^{-\xi_p r}$ ($n = 1, \ldots, 8$); the radial d-type functions were $r^n e^{-\xi_d r}$ ($n = 2, \ldots, 9$). Combining representations of $\bar{H}_{QQ}$ in the s, s-p, and s-p-d limits with the static-exchange representations of $\bar{H}_{PP}^0$ and $\bar{H}_{PP}$ of Sec. III A 1, the results of Fig. 3 were obtained using the same rational-fraction fitting points as in the radial-limit calculation. Convergence was found to be good in the s-p limit. The stability
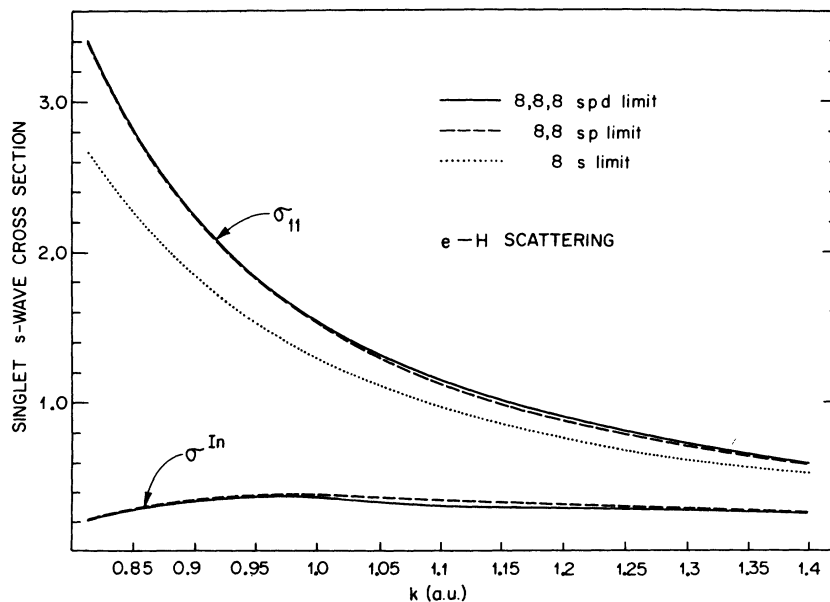

FIG. 3. Singlet s-wave elastic e-H cross section with the optical potential $\bar{H}_{QQ}$ calculated in the s, s-p and s-p-d limits, with eight Slater functions of each symmetry and full CI's performed in each case. The total inelasticity is given for the s-p and s-p-d limits. Convergence is good over the whole energy region, indicating that for this energy range, orbital basis functions of f and higher symmetries are probably not needed for calculation of the elastic amplitude and/or total inelasticity. Cross sections are in units of πa_0^2, statistical factor of $\frac{1}{4}$ not included. The complete s, s-p, s-p-d calculations took 33, 121, and 291 sec (from the start) respectively, on a CDC-6400 computer.

TABLE III. Radial-limit singlet s-wave elastic cross sections (πa_0^2). Seven s-type Slater functions in addition to ϕ_{1s} were used to form pseudostates. These functions were of the form $r^n e^{-\xi_s r}$, $n = 1, \ldots, 7$. Computations are shown for three choices of ξ_s. (Cross sections do not include the statistical weight of $\tfrac{1}{4}$.)

| | Fredholm[a] | | | Burke and Mitchell[b] | Heller and Yamani[c] |
k (a.u.)	$\xi_s = 0.8$	$\xi_s = 1.0$	$\xi_s = 1.2$	4 s states	10 s states
0.875	2.012	2.027	2.023		
0.90	1.833	1.835	1.849		
1.0	1.301	1.288	1.325	1.312	1.383
1.1	0.974	0.961	0.995	0.916	0.980
1.2	0.763	0.761	0.773		
1.3	0.622	0.627	0.625	0.616[d]	0.644[d]
1.4	0.523	0.533	0.520	0.529[e]	0.542[e]

[a] The fitting points for the rational-fraction wave (Rek, Imk) $= (0.88, 0.06)$, $(0.93, 0.07)$, $(1.0, 0.083)$, $(1.1, 0.10)$, $(1.2, 0.11)$, and $(1.5, 0.14)$, giving a [2, 3] rational continuation. A rotation angle of $\phi = \pm 0.1$ radians was used to calculate D^{opt} $(E + i\epsilon)$ and D_{1s}^{opt} $(E + i\epsilon)$.
[b] Reference 2.
[c] Reference 4.
[d] $k = 1.304$ a.u. $(k^2 = 1.7)$.
[e] $k = 1.414$ a.u. $(k^2 = 2.0)$.

of the results to variation of the nonlinear parameter ξ_p, used in defining the p-type Slater function, is shown in Fig. 4, and was found to be good for a large range of ξ_p spanning the actual target size. Similar studies showed that the s-p-d limit results were insensitive to variations of ξ_d over a wide range of values centered at about 1.6. Final elastic-scattering results and total inelasticities are presented in Fig. 5, where they are compared with the T-matrix extrapolation results of McDonald and Nuttall,[5] the close-coupling plus correlation results of Burke and Taylor,[1] and the close-coupling pseudostate results of Callaway and Wooten.[3] Based on the stability of the numerical results with regard to change in basis size and variations of nonlinear parameters, we estimate that the results should be good to ~5% over the range $k = 1.0$–1.4. Convergence, for complex z, of $V^{\mathrm{opt}}(z)$ itself was much better than 5%, with interpolation for dispersion correction and the subsequent extrapolation computation $V^{\mathrm{opt}}(E + i\epsilon)$ accounting for most of the error. Unfortunately, we know of no rigor-
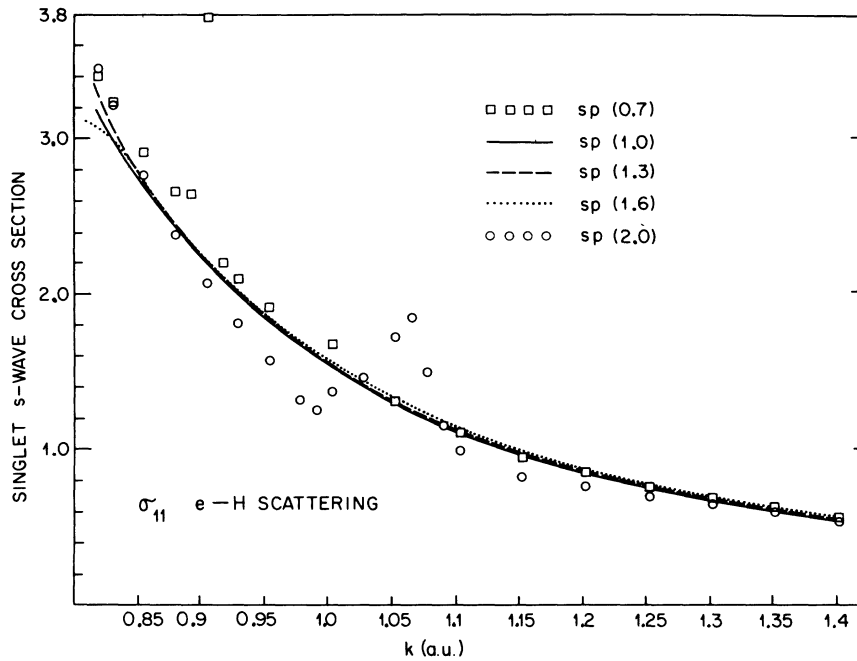

FIG. 4. Singlet s-wave e-H elastic-scattering cross section (in units of πa_0^2, statistical factor of $\tfrac{1}{4}$ not included) in the s-p limit as a function of the nonlinear parameter ξ_p ($\chi_i^p = r^{n+1} e^{-\xi_p r}$, $n = 0, \ldots, 7$) defining the scale of the Slater-type p basis orbitals. The value of ξ_s (the exponent of the s-type states $\chi_i^s = r^n e^{-\xi_s r}$, $n = 0, \ldots, 7$) is 1.0, and the value of ξ_p is shown in parentheses. For $\xi_p = 1.0$, 1.3, and 1.6, convergence is excellent over the whole energy range from $k = 0.825$ to 1.4 a.u. For $\xi_p = 0.7$, the basis becomes diffuse and begins to describe the lowest ^1S resonance, which occurs here at $k \simeq 0.9$, a little above its expected value. For values much smaller than $\xi_p = 0.7$, the diffuse basis does not couple strongly with the $1s$ ground state of H, and thus correlation is not well described. For $\xi_p = 2.0$, the poles of $\bar{H}_{QQ}$ have begun to spread out to the point that rational continuation no longer yields reasonable results.

ous way to bound the error inherent in either the calculations of $V^{opt}(z)$ or in the extrapolation procedure.

B. Singlet p-wave cross section

The correlated singlet p-wave e-H cross section at intermediate energies was found to be very small. This made the complex-basis-function technique unsatisfactory for two reasons: First, the rational-fraction technique generally does not give results stable to more than two decimal places; as this result is roughly independent of the actual magnitude of the (complex) phase of the determinants, small cross sections are difficult to calculate. Second, the systematic error inherent in use of the complex-basis technique becomes a dominating factor for very small cross sections. Both of these problems could be overcome by use of larger static-exchange basis sets; however, this would entail accurate calculations of Laguerre-type matrix elements, which at present are not readily available.[23] The result of these problems is that well-converged continuation results were not obtained, and an alternate technique for calculating the substituted determinants was used.[24]
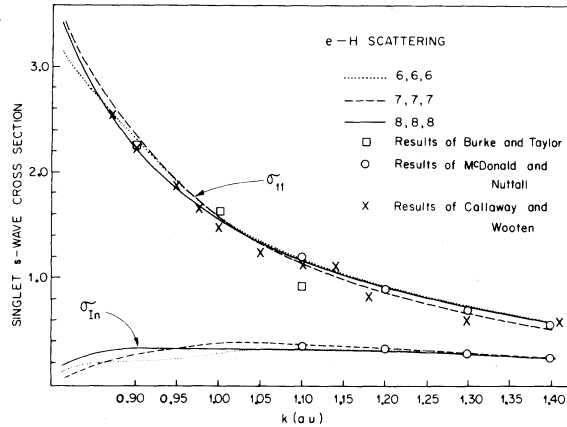
FIG. 6. Plots of $D^{opt}(z)$ and $D_{1s}^{opt}(z)$ as a function of Imz, for fixed values of Rez, for p-wave singlet e-H scattering. These nearly linear plots were extrapolate (using a linear least-squares procedure) to give $D^{opt}(E + i\epsilon)$ and $D_{1s}^{opt}(E + i\epsilon)$.

FIG. 5. Singlet s-wave cross section for e-H elastic scattering, the total inelasticity as computed in the s-p-d limit with differing number of basis functions of s, p, and d symmetry. Fredholm results are shown for (6, 6, 6), (7, 7, 7), and (8, 8, 8) calculations, with $\xi_s = 1.0$, $\xi_p = 1.3$, and $\xi_d = 1.6$ where a full CI was performed for H_{QQ} in each case. Also shown are the close-coupling plus correlation results of Burke and Taylor (Ref. 1), close-coupling (s-p limit) results of Callaway and Wooten (Ref. 3), and the T-matrix extrapolation results of McDonald and Nuttall (Ref. 5). Within the estimated convergence of the method, the results seem to be in reasonable agreement. The (8, 8, 8) calculation took 291 sec (from the start on a CDC-6400 computer) for computation of the entire curve shown. The cross section is in units of πa_0^2, and the statistical factor of $\frac{1}{4}$ is not included.
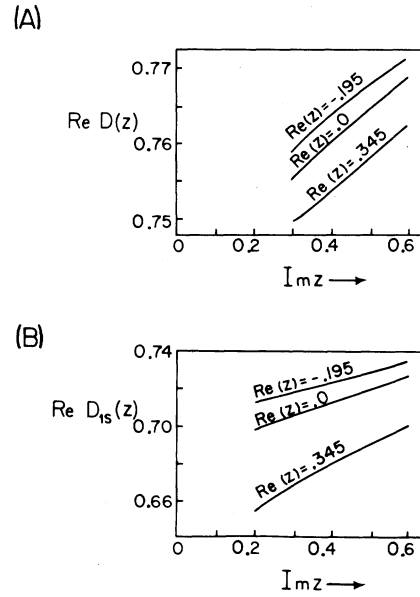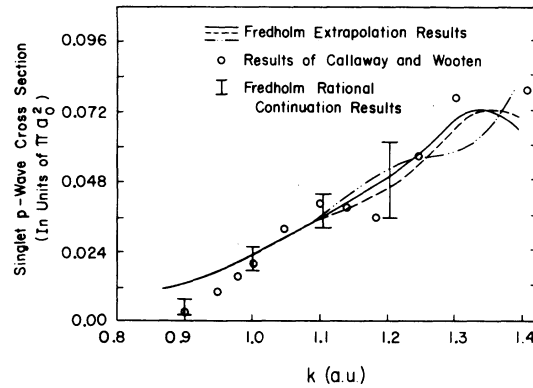
FIG. 7. Singlet p-wave e-H cross section at intermediate energies (in units of πa_0^2, but not including the statistical factor $\frac{1}{4}$) as calculated by the Fredholm extrapolation method and by Fredholm rational-fraction continuation (using complex basis functions). The Fredholm extrapolation results are the results of three different s-p-d limit calculations, and have converged reasonably well. As indicated by the error bars, convergence of the rational-fraction–complex-basis-function calculations was much less satisfactory. As in the s-wave case, the pseudostate (s-p limit) close-coupling results of Callaway and Wooten (Ref. 3) are in general agreement with the Fredholm results, except near $k = 1.2$ a.u., where the close-coupling results give a fairly broad pseudoresonance.

Plots of

$$\overline{D}^{\text{opt}}(z) = \det\left\{\left[z - z\overline{\Delta} - \overline{H}_{PP} - \overline{H}_{PQ}\left(\frac{1}{z - \overline{H}_{QQ}}\right)\overline{H}_{QP}\right]\Big/\left(z - \overline{H}_{PP}^0\right)\right\}$$

and

$$\overline{D}_{1s}^{\text{opt}}(z) = \det\left\{\left[z^* - z^*\overline{\Delta} - \overline{H}_{PQ} - \overline{H}_{PQ}\left(\frac{1}{z - \overline{H}_{QQ}}\right)\overline{H}_{QP}\right]\Big/\left(z^* - \overline{H}_{PP}^0\right)\right\}$$

in the complex z plane revealed that they were both smooth and nearly linear in Imz, for fixed Rez.[25] This is shown in Fig. 6. The $z \to E + i\epsilon$ limit of $\overline{D}^{\text{opt}}(z)$ and $\overline{D}_{1s}^{\text{opt}}(z)$ was then taken by direct extrapolation in Imz, thus avoiding use of complex basis functions and of rational continuations. Results of three such extrapolations are shown in Fig. 7, where the singlet p-wave cross section is given, and are compared with Fredholm continuation results[26] and with the pseudostate close-coupling results of Callaway and Wooten.[3]

C. Singlet angular distributions

The singlet e-H angular distribution for $E = 13.6$ and 16.5 eV calculated using s and p waves only is given in Fig. 8, where the present results are compared with the s-p angular distribution obtained from the $1s$-$2s$-$2p$ calculation of Burke, Schey, and Smith.[27] Comparison of the $1s$-$2s$-$2p$ close-coupling results for the partial waves for $l = 2, 3, 4,$ and 5 with pseudostate close-coupling results[28] suggests that the $l = 2, \ldots, 5$ partial-wave singlet amplitudes are not strongly affected by further correlation, implying that the flux into higher excited states from these partial waves
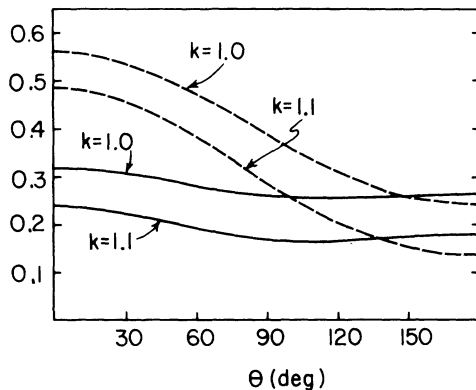
is small, and perhaps may be neglected. Under this assumption, we have calculated the singlet elastic angular distribution (Fig. 9) at $E = 13.6$ and 16.5 eV using the s-wave and p-wave amplitudes from the present calculation (i.e., the amplitudes corresponding to the s and p cross sections of Figs. 6 and 8) combined with the $l = 2, 3, 4,$ and 5 partial-wave amplitudes from the $1s$-$2s$-$2p$ close-coupling calculations of Burke, Schey, and Smith.[27] This angular distribution is compared with that predicted by the $1s$-$2s$-$2p$ close-coupling results for all the singlet partial waves. It is evident that inclusion of highly excited channels and ionization channels has an important effect on the elastic cross section.
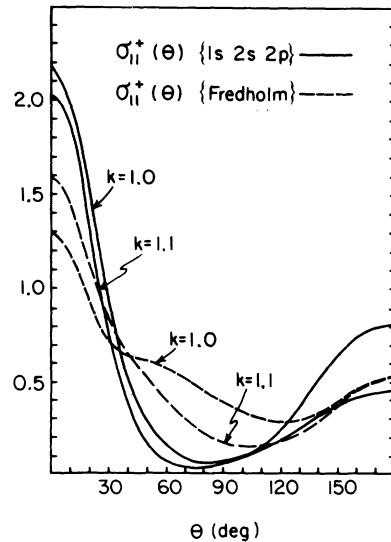

FIG. 8. Elastic singlet angular distributions for e-H scattering (cross section in units of πa_0^2, omitting the statistical factor of $\frac{1}{4}$) computed using the s and p amplitudes corresponding to the results of Figs. 5 and 7 (broken lines). The results are compared with the angular distribution predicted using the s and p amplitudes (solid lines) from the $1s$-$2s$-$2p$ close-coupling amplitudes of Burke, Schey, and Smith (Ref. 27).

FIG. 9. Angular distribution for singlet e-H scattering. The solid lines are the results predicted from the $1s$-$2s$-$2p$ calculation (using partial waves $l = 0, 1, \ldots, 5$) of Burke, Schey, and Smith (Ref. 27) at $k = 1.0$ and 1.1 a.u. The broken lines are the result of taking the s- and p-wave amplitudes from the Fredholm work, and coupling them with the $l = 2, 3, 4,$ and 5 amplitudes of Burke, Schey, and Smith. As discussed in the text, the $l = 2, 3, 4,$ and 5 amplitudes are not expected to be strongly influenced by correlation, or contribute strongly to the total inelasticity. The cross section is in units of πa_0^2 and does not include the statistical weight of $\frac{1}{4}$.

IV. SUMMARY AND DISCUSSION

Singlet elastic e-H cross sections and angular distributions have been calculated in the intermediate energy region (10–27 eV) using a Fredholm technique in conjunction with an inelastic optical potential. Based on this work, we draw several conclusions.

(i) The elastic angular distribution is sensitive to flux into highly excited channels and ionization channels.

(ii) The agreement of the pseudostate close-coupling work of Burke and Mitchell,[2] Callaway and Wooten,[3] and Heller and Yamani[4] with the present Fredholm results suggests that pseudostate techniques may be used to compute average cross sections at energies where large numbers of channels are open, thus allowing their use in a much wider variety of situations than had been earlier anticipated.

(iii) Many-body inelastic optical potentials, de-scribing the average flux into a continuum of open channels, may be calculated by performance of a standard bound-state configuration interaction. (This latter result is, of course, implied in the T-matrix work of Schlessinger,[29] Nuttall,[5,30] and their co-workers; the advantage of the Fredholm determinant lies in its better behavior as a function of complex energy.[31])

ACKNOWLEDGMENTS

*Preliminary versions of the results contained here were presented at the Numerical Methods in Atom-Electron Collisions Conference, Paris, France, 1973 (unpublished), and at the Seventh International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973 (unpublished).

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[23]For the calculations reported, the Laguerre basis was

generated by direct diagonalization of the Slaters; in CDC single precision (60 bits) this proved to be unstable for more than 14 functions. Progress in direct performance of Laguerre integrals has been made by L. Fishman (unpublished).

[24]The authors thank T. S. Murtaugh for many helpful discussions about extrapolation techniques.

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