sured with the 32-keV K x rays. The inherent resolution of the system at larger proton energy losses is expected to be better than the 19% resolution observed with the 32-keV K x rays.

In Table IV, we compare values of experimental and theoretical parameters from our measurements at proton energies of 66 and 100 MeV with the values obtained from previous work at proton energies from 31.5 to 80 MeV.

IV. CONCLUSIONS

We have observed energy-loss distributions of 66- and 100-MeV protons traversing a proportional counter filled with 11.0 mg/cm^2 of a gas mixture of 90% xenon plus 10% methane. The measured distributions are consistent with the theoretical distribution functions obtained from the theory of Vavilov[4]; however, the observed distributions do not agree with the formulation of Shulek *et al.*,[8] which extends the Vavilov theory to include binding effects of the atoms of the absorber.

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Fredholm Optical-Potential Calculation of Elastic Electron–Hydrogen-Atom Phase Shifts

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A Fredholm technique is used to compute elastic phase shifts for electron–hydrogen-atom scattering using the Feshbach optical potential. The method is noniterative and is computationally highly efficient as it allows computation of the Fredholm determinant $D(E+i\epsilon)$ at a series of energies from a single set of matrix elements of the optical potential. Scattering information is then obtained over a continuous range of energies by interpolation of $D(E+i\epsilon)$; resonance is easily located by inspection of the zeros of $\mathrm{Re}D(E+i\epsilon)$.

I. INTRODUCTION

Elastic optical potentials[1,2] provide a formal technique for reduction of a many-channel problem to a one-channel problem. The Feshbach projection technique for construction of optical potentials for elastic electron and positron scattering from atomic and molecular systems has been used to determine approximate resonance energies[3] and widths[4] and, more recently, phase shifts.[5–7] An alternate approach, based on the fact that the self-energy of many-body Green's-function theory also acts as an optical potential[2,8] has been used to discuss elastic[9,10] and inelastic[11] electron- and positron-atom scattering.

Use of an optical potential eliminates the need for solving large sets of coupled equations. An accurate optical potential for electron-atom scattering, however, may contain a large number of nonlocal and energy-dependent terms. Several techniques have been used for extracting scattering information from such potentials. These include the distorted Born approximation,[9] iteration,[7] coupled-equation methods,[5] and the noniterative technique of Percival and Marriott.[6,12]

Alternatively, one may use an "analytic" or basis-set expansion such as that of Harris.[13] Since only matrix elements of the optical potential are required, its nonlocality causes no special difficulty. A disadvantage of this type of method, however, is that scattering information is obtained only at certain fixed energies from a single computation.[13,14] Another approach which shares the advantages of the Harris-type methods but gives accurate scattering information over a range of energies is the "R-matrix" method, which has recently been investigated in the context of electron-atom[15] and nuclear[16] scattering.

It is the purpose of this paper to show that accurate scattering information may be easily constructed directly from an elastic optical potential by means of the Fredholm method.[17] The method is noniterative and simple and rapid enough so that large expansion basis sets can be employed. Since large expansions can be used, the problem of determining optimal pseudostates, which arises in the pseudostate[18] modification of the close-coupling method, is avoided. Additionally, exploitation of the analytic properties of the Fredholm determinant[19] allows highly accurate interpolation of scattering information from knowledge of the determinant at relatively few points on the real energy axis; resonances are easily located by interpolating to find the zeros of the real part of the determinant.

We apply the method to the model problem of elastic s-wave electron–hydrogen-atom scattering. Section II contains a discussion of the construction of the optical potential. The construction, analyticity, and interpolation of the Fredholm determinant are discussed in Sec. III, where it is pointed out that once the determinant has been computed at one energy, extension to all energies takes a relatively small additional amount of computation time. In Sec. IV we discuss selection of the basis set, and present results for the s-wave singlet and triplet scattering. A brief discussion is given in Sec. V.

II. CONSTRUCTION OF OPTICAL POTENTIAL

For elastic s-wave electron-hydrogen scattering at energies below the first excitation threshold, the standard Feshbach[1] procedure yields the following one-particle Schrödinger equation (atomic units are used throughout):

$$\left[-\tfrac{1}{2}\nabla_1{}^2+V^{\pm}_{\mathrm{se}}(1)+V^{\pm}_{\mathrm{opt}}(1,E)\right]\psi^{\pm}_E(1)=(E-E_{1\mathrm{s}})\psi^{\pm}_E(1)\ . \tag{2.1}$$

The +(−) refers to singlet (triplet) scattering. E is the total energy of the scattering system and E_{1s} is the energy of the hydrogen ground state, $V^{\pm}_{\mathrm{se}}$ is the usual static-exchange potential,[20] and the Feshbach optical potential in spectral expansion form is

$$V^{\pm}_{\mathrm{opt}}(1,E)=2\sum_i\frac{\left(\psi_{1s}(2)\,|1/r_{12}|\,\varphi^{\pm}_i(1,2)\right\rangle\left\langle\varphi^{\pm}_i(1,2)|\,1/r_{12}|\,\psi_{1s}(2)\right)}{E-E^{\pm}_i}\ . \tag{2.2}$$

In Eq. (2.2), the boldface parentheses denote integration over coordinate two only, ψ_{1s} is the $1s$ hydrogen orbital and

$$(E^{\pm}_i-H_{QQ})\,\varphi^{\pm}_i(1,2)=0\ , \tag{2.3}$$

where H is the full Hamiltonian and Q is the usual properly symmetrized Feshbach projector[21] which maintains the strong orthogonality of $\varphi^{\pm}_i(1,2)$ to ψ_{1s}. The states $\varphi^{\pm}_i(1,2)$ have total orbital angular momentum $L=0$ and total spin $S=0$ (+) or $S=1$ (−).

Equation (2.3) may be solved by the configuration-interaction method. First an orthonormal one-particle basis set is selected, H_{QQ} is then diagonalized in the set of all symmetry-adapted two-electron configurations constructed from the basis functions. The one-electron basis chosen here consisted of the pseudo-hydrogen-atom orbitals obtained by diagonalizing the hydrogen-atom Hamiltonian in the Slater set

$$\chi^{\xi_l}_{n_l}(\vec{\mathrm{r}})=\frac{(2\xi_l)^{n+l+1/2}}{[(2n+2l)!]^{1/2}}\;r^{n+l-1}e^{-\xi_l r}\,Y_{l0}(\Omega_r)\ . \tag{2.4}$$

For basis sets used here ($n\leqslant 9$) only the first few pseudo-hydrogen functions resemble the true hydrogen orbitals. The rest describe the effect of bound excited states and the continuum. The projector Q in Eq. (3) is taken in account by excluding configurations containing the pseudo-$1s$ orbital. If $\xi_s=1.0$, the calculated phase shifts must converge monotonically from below as the one-particle basis set is increased.[22] For $\xi_s\neq 1.0$, the lower-bound principle no longer rigorously holds;

empirically it was always found to be obeyed since the true- and pseudo-1s functions differ only negligibly for basis-set sizes and values of ξ_s used.

The main computational labor involved in the construction of $V^{\pm}_{\mathrm{opt}}(1, E)$ is the determination of the eigenvectors and eigenvalues of H_{QQ}; once this has been done the optical potential may be calculated rapidly at any energy. Once $V^{\pm}_{\mathrm{opt}}(1, E)$ is known the scattering phase shift may be computed by construction of the Fredholm determinant.

III. CONSTRUCTION, ANALYTIC PROPERTIES, AND INTERPOLATION OF FREDHOLM DETERMINANT

A. Numerical Computations of Fredholm Determinant

Numerical techniques for construction of the Fredholm determinant for local, nonlocal, and energy-dependent potentials have been given previously[17]: Introduction of a set of N quadrature points and weights k_i and w_i allows us to write, for an arbitrary potential V,

$$D(k_0)=\prod_{i=1}^{N}\frac{1}{\frac{1}{2}k_0^2-\frac{1}{2}k_i^2}\,D'(k_0)\,, \tag{3.1}$$

where

$$D'(k)=\begin{vmatrix} & & +i\pi\tilde{V}_{10} \\ & \underline{\mathrm{d}}' & \vdots \\ & & i\pi\tilde{V}_{N0} \\ -\tilde{V}_{01} & \cdots \quad -\tilde{V}_{0N} & 1+i\pi\tilde{V}_{00} \end{vmatrix}\,, \tag{3.2}$$

with

$$(\underline{\mathrm{d}}')_{ij}=(\tfrac{1}{2}k_0^2-\tfrac{1}{2}k_i^2)\delta_{ij} - (w_i k_i)^{1/2}\langle k_i|V|k_j\rangle(w_j k_j)^{1/2}\,, \tag{3.3a}$$

$$\tilde{V}_{0i}=\langle k_0|V|k_i\rangle(w_i k_i)^{1/2}\,, \tag{3.3b}$$

and

$$\langle k_i|V|k_j\rangle=\frac{2}{\pi}(k_i k_j)^{1/2}\int_0^\infty dr\,r^2 j_l(k_i r) \times V(r) j_l(k_j r) \tag{3.4}$$

while $\frac{1}{2}k_0^2$ gives the kinetic energy. The finite-dimensional determinant $D(k_0)$ is the approximate lth partial-wave Fredholm determinant $\det[1-G_l^0(k_0)V]$ whose phase allows evaluation of approximate S-matrix elements as

$$S(k_0)=e^{2i\delta(k_0)}=D(k_0)^*/D(k_0)\,.$$

Equations (3.1) and (3.2) effectively sum the expansion

$$D(k_0)=1+P\int_0^\infty\frac{A(E')\,dE'}{\frac{1}{2}k_0^2-E'}-i\pi A(\tfrac{1}{2}k_0^2)\,, \tag{3.5}$$

where

$$A(\tfrac{1}{2}k_0^2)=-\langle k_0|V|k_0\rangle+\cdots+\frac{(-1)^{n+1}}{n!}\int_0^\infty\frac{dE_1\cdots dE_n}{(\frac{1}{2}k_0^2-E_1)\cdots(\frac{1}{2}k_0^2-E_n)}\begin{vmatrix}\langle k_0|V|k_0\rangle\cdots\langle k_0|V|E_1\rangle \\ \vdots \\ \langle E_n|V|k_0\rangle\cdots\langle E_n|V|E_n\rangle\end{vmatrix}+\cdots\,. \tag{3.6}$$

The expansion of $A(\frac{1}{2}k_0^2)$, in spite of first appearances, does not involve any singular integrals; however the principal value integral of Eq. (3.5) requires careful placement of k_0 with respect to the quadrature points k_i. It is not difficult to show that for N given quadrature points and weights that there are $(N-1)$ values of k_0 (one between each two consecutive k_i) for which the principal value integral of Eq. (3.5) is accurately performed.[23] Thus once the $N\times N$ matrix (3.2) has been computed one can compute $D(k_0)$ for $(N-1)$ values of k_0 without recomputation of the N^2 matrix elements of V. This is an important consideration as computation of the matrix elements $\langle k_i|V^{\pm}_{\mathrm{opt}}(1,E)|k_j\rangle$ is time consuming. Given the value of $D(k_0)$ at $(N-1)$ values of k_0 we can interpolate to find $D(k)$ over a continuous range of k.

B. Point-Wise Rational-Fraction Interpolation

Interpolation of the determinant $D(k)$ between known values of k may be carried out using a point-wise rational-fraction technique which was introduced by Schlessinger[24] for analytic continuation of off-shell T-matrix elements, and more recently has been used for continuation and interpolation of the Fredholm determinant.[19] The method finds the rational fraction

$$R_{[N,M]}(x)=P_N(x)/Q_M(x)\,, \tag{3.7}$$

where

$$P_N(x)=\sum_{i=0}^{N}p_i x^i\,, \tag{3.8a}$$

$$Q_M(x)=1+\sum_{i=1}^{M}q_i x^i\,, \tag{3.8b}$$

such that $R_{[N,M]}(x_i) = D(x_i)$ at $(N+M+1)$ points x_i. $R_{[N,N]}(x)$ is easily determined recursively from a continued-fraction representation[24] and provides a highly accurate and rapidly convergent interpolation alogarithm.

C. Analytic Properties of Fredholm Determinant

For local potentials the partial-wave Fredholm determinant is identified with the corresponding Jost[25] function and thus has well-known analytic properties. For potentials satisfying the conditions[25]

$$\int_0 r\,|V(r)| < \infty\,, \tag{3.9a}$$

$$\int^{\infty} |V(r)| < \infty\,, \tag{3.9b}$$

$D(k)$ is analytic in the upper $\frac{1}{2}k$ plane and possesses at least a continuous derivative for real k ($k \neq 0$).

For our case, however, the potential goes asymptotically as[26] $-\alpha/2r^4$, α being the polarizability and for $k \neq 0$ it can be shown that $D(k)$ possesses at least a continuous second derivative for real k.[27]

The fact that the potentials $V_{\mathrm{se}}^{\pm}$ and $V_{\mathrm{opt}}^{\pm}$ are nonlocal does not weaken the above assertion that $D(k)$ should have at least a continuous second derivative for real k. This may be seen by considering the fact that the nonlocal parts of the potential are of the form

$$U(r_1 r_2) = e^{-\beta_1 r_1} \frac{1}{|r_1 - r_2|} e^{-\beta_2 r_2}\,, \tag{3.10}$$

with β_1, β_2 real and positive. It is not difficult to verify that for such a nonlocal potential that the conditions[28]

$$\mathrm{tr}[(G^0 U)^n] < \infty\,, \quad n = 1, 2, \ldots \tag{3.11a}$$

$$\mathrm{tr}[\,|G^0 U|\,] < \infty \tag{3.11b}$$

necessary for the absolute convergence of the expansion of the Fredholm determinant may be strengthened by finding a uniform bound (in k) to $|G^0(k)U|$ in a region including the real k axis thus giving *uniform* convergence of the expansion. As the individual traces can be shown to be analytic in k in a similar region it may be seen that the Fredholm determinant is analytic for real k for nonlocal potentials of the form of Eq. (3.10), namely, those which are exponentially bounded in both variables. We thus conclude that the long-range tail of $V_{\mathrm{opt}}^{\pm}$ rather than its nonlocality, limits the differentiability of $D(k)$, for real k.[29]

Note added in proof. The technique of Regge (Ref. 25, p. 337) may be used to show that, as the potentials are analytic functions of a complex coordinate, $D(k)$ is in fact, analytic for real k.

D. Interpolation of Scattering Data

Since the Fredholm determinant has at least two continuous derivatives for real k and since the S matrix is given by

$$S(k) = e^{2i\delta(k)} = \frac{D(E+i\epsilon)^*}{D(E+i\epsilon)} = \frac{D(k)^*}{D(k)}\,, \tag{3.12}$$

resonances arise computationally as complex zeros of $D(k)$ [rather than as poles of $S(k)$]. Thus it is clear that scattering information is easily interpolated via the determinant. Previous computations[19] have shown that the Fredholm determinant is, in practice, very smooth even in regions where $S(k)$ is a rapidly varying function of the energy. Narrow resonances are located by inspecting the zeros of $\mathrm{Re}[D(E+i\epsilon)]$ noting that at such zeros, resonance half-widths $\frac{1}{2}\Gamma$ are given by

$$\frac{\Gamma}{2} = \left.\frac{\mathrm{Im}\,[D(E+i\epsilon)]}{(d/dE)\,\mathrm{Re}[D(E+i\epsilon)]}\right|_{E=E_{\mathrm{res}}}. \tag{3.13}$$

E. Small Complication Arising from Use of Optical Potential

Using an optical potential, even for elastic scattering, requires care if the analytic properties of the Fredholm determinant are to be maintained. A two-channel example will make this clear.[17] Consider

$$\begin{aligned} D(E+i\epsilon) &= \det\left(\begin{array}{c:c} 1 - G_{11}^0 V_{11} & -G_{11}^0 V_{12} \\ \hdashline -G_{22}^0 V_{21} & 1 - G_{22}^0 V_{22} \end{array}\right) \\ &= \det(1 - G_{11}^0 V)\,\det(1 - G_{22}^0 V_{22}) \\ &\quad \times \det(1 - \mathcal{G}_{11} V_{12} \mathcal{G}_{22} V_{21})\,, \end{aligned} \tag{3.14}$$

where

$$\mathcal{G}_{ii} = (1 - G_{ii}^0 V_{ii})^{-1} G_{ii}^0\,. \tag{3.15}$$

In the case of elastic scattering with channel 2 closed, scattering information may be obtained from the quantity

$$\begin{aligned} D^{\mathrm{opt}}(E+i\epsilon) &= \det(1 - G_{11}^0 V_{11})\,\det(1 - \mathcal{G}_{11} V_{12} \mathcal{G}_{22} V_{21}) \\ &= \det[1 - G_{11}^0 (V_{11} + V_{12} \mathcal{G}_{22} V_{21})] \end{aligned} \tag{3.16}$$

as the factor $\det(1 - G_{22}^0 V_{22})$ is real if channel 2 is closed and thus does not affect the phase.

This is equivalent to what is usually done in optical-potential calculations. However, omission of the factor $\det(1 - G_{22}^0 V_{22})$, which may have zeros below the inelastic threshold, may destroy the analytic properties desired for interpolation. Thus, for example, while $D(E+i\epsilon)$ has a continuous second derivative for the s-wave scattering of electrons from hydrogen, $D^{\mathrm{opt}}(E+i\epsilon)$ has poles on the real axis corresponding to the compound-state resonances; these poles are cancelled by the real factor $\det(1 - G_{22}^0 V_{22})$ which is necessary to en-

TABLE I. Convergence of the s-wave singlet electron-hydrogen phase shift in the s, s-p, and s-p-d limits for the unoptimized choice $\xi_s = \xi_p = \xi_d = 1.0$. The triples of numbers (n_s, n_p, n_d) refer to the number of s-, p- and d-type atomic Slater functions used in the diagonalization of H_{QQ}.

k (a.u.)	(3,0,0)	(6,0,0)	(9,0,0)	(6,6,0)	(6,8,0)	(6,6,3)	(6,6,6)
0.2	1.8948	1.8970	1.8973	2.0535	2.0546	2.0607	2.0618
0.4	1.2673	1.2693	1.2696	1.4024	1.4033	1.4092	1.4104
0.6	0.9083	0.9102	0.9105	1.0286	1.0291	1.0348	1.0362
0.8	0.7218	0.7256	0.7261	0.8736	0.8750	0.8789	0.8807

sure that the computed determinant be easily interpolated.

IV. CALCULATIONS AND RESULTS

A. Nonresonant Phase Shifts

The calculations reported here were performed mainly to determine whether the combination of optical-potential and Fredholm techniques is efficient and simple enough to make application to larger systems possible. It was thus important to determine whether moderate-size nonoptimized basis sets could yield good nonresonant phase shifts. For this reason, and for computational simplicity, the Slater basis functions were constrained to have only one orbital exponent per symmetry.

Calculations of the nonresonant singlet and triplet phase shifts were performed with the exponent choice $\xi_s = \xi_p = \xi_d = \xi_f = 1.0$. This choice was made since then the eigenfunctions of H_{QQ} have the same scale as the 1s hydrogen orbital. This guarantees strong coupling (the optical potential can be represented as a relatively small sum over states) and a good representation of short-range correlation. This choice also gives an exact representation of the long-range multipole polarization forces arising from induced multipoles of order 2^l,[30] with l being the highest single-particle angular momentum included in the basis set.

Table I shows convergence of the singlet s-wave phase shift as a function of the number of basis functions in the first three angular limits. Inclusion of functions of f symmetry probably increases the phase shifts by no more than 0.002 rad. Table II compares several calculations with the results of a static-exchange calculation and the "exact" results of Schwartz.[31] The (6, 6, 6), (6, 8, 6), and (6, 6, 6, 3) results[32] show that the computations have converged to the "exact" results within a few tenths of a percent. Although the phase shifts are only shown for those values of k where they may be compared with known results, the rational-fraction interpolation which generated them also implicitly contains the elastic phase shift over the whole elastic region; thus no new computational work would be involved to construct $\delta(k)$ for new values of k. These results are compared with a (6, 6, 6) computation with the exponent choice $\xi_s = 0.802$, $\xi_p = 1.45$, and $\xi_d = 1.803$. These latter exponents were used in an "optimal" pseudostate calculation.[33] The results indicate that in calcula-

TABLE II. Singlet[a] s-wave electron-hydrogen phase shifts in the s, s-p, s-p-d and s-p-d-f limits. The "exact" results of Schwartz and the static-exchange results are shown for comparison at a set of representative energies; the interpolation yielded results at all values of k. The quadruples (n_s, n_p, n_d, n_f) indicate the number of s, p, d, f atomic Slater functions employed in diagonalizing H_{QQ}. We note that the (2,2,2,2) basis set gives the lowest three multipole polarization forces correctly.

k (a.u.)	Static exchange	"Exact"	(6,8,6,0)[b]	(6,6,6,3)[b]	(6,6,6,0)[b]	(6,6,6,0)[c]	(2,2,2,2)[b]
0.1	2.399	2.553	2.5493	2.5480	2.5473	2.5443	2.5380
0.2	1.870	2.067	2.0628	2.0627	2.0618	2.0573	2.0457
0.3	1.508	1.696	1.6923	1.6929	1.6920	1.6892	1.6727
0.4	1.239	1.415	1.4113	1.4112	1.4104	1.4098	1.3896
0.5	1.031	1.202	1.1967	1.1969	1.1962	1.1958	1.1732
0.6	0.869	1.041	1.0367	1.0368	1.0362	1.0354	1.0097
0.7	0.744	0.930	0.9264	0.9260	0.9254	0.9251	0.8907
0.8	0.651	0.886	0.8821	0.8811	0.8807	0.8802	0.8122

[a] These results were presented at the Seventh International Conference on Electronic and Atomic Collisions, Amsterdam, 1971.

[b] All orbital exponents are 1.0

[c] $\xi_s = 0.802$, $\xi_p = 1.45$, $\xi_d = 1.803$, as discussed in the text.

TABLE III. Triplet[a] s-wave electron-hydrogen phase shifts in the s, s-p, and s-p-d limits. The "exact" results of Schwartz (Ref. 31) and the static exchange results are shown for comparison at a representative set of k values; the interpolation yielded results for all k. The notation is that of Tables I and II. All ξ were 1.0.

k (a.u.)	Static Exchange	"Exact"[b]	(6, 6, 6)	(6, 6, 0)	(6, 0, 0)
0.1	2.9076	2.9388	2.9347	2.9338	2.9077
0.2	2.6792	2.7171	2.7166	2.7153	2.6794
0.3	2.4611	2.4996	2.4984	2.4970	2.4616
0.4	2.2573	2.2938	2.2930	2.2916	2.2579
0.5	2.0701	2.1046	2.1038	2.1024	2.0710
0.6	1.9016	1.9329	1.9318	1.9306	1.9019
0.7	1.7488	1.7797	1.7784	1.7772	1.7506
0.8	1.614	1.643	1.6430	1.6419	1.6166

[a] These results were presented at the Seventh International Conference on Electronic and Atomic Collisions, Amsterdam, 1971.

[b] C. Schwartz, Ref. 31.

TABLE IV. Convergence of the s-wave singlet phase shifts for the exponent choice $\xi_s = 0.5$, $\xi_p = \xi_d = 1.0$. The notation is that of Tables I and II.

k (a.u)	(3, 0, 0)	(9, 0, 0)	(6, 6, 0)	(6, 8, 0)	(6, 6, 3)	(6, 6, 6)
0.2	1.8845	1.8965	2.0525	2.0536	2.0597	2.0608
0.4	1.2521	1.2687	1.4011	1.4020	1.4079	1.4091
0.6	0.8854	0.9095	1.0270	1.0275	1.0332	1.0346
0.8	0.6909	0.7249	0.8722	0.8737	0.8775	0.8793

tions of the present type, where basis sets of intermediate size do not cause computational difficulty, exponent optimization seems unnecessary; this is of course not the case for very small expansions. The (2, 2, 2, 2) calculation with all $\xi_l = 1.0$ is of interest since it exactly reproduces the first three multipole polarization forces.[30] This very restricted basis yields a large part of the correlation phase shift. Whether this is due primarily to the basis set's correct description of polarization or its approximate representation of short-range correlation is unclear. It is clear, however, that polarization alone is not sufficient to describe the low-energy scattering. Table III gives the computed s-wave triplet phase shifts. In this case correlation contributes only a small fraction to the total phase shift and extensive basis-set studies were not performed.

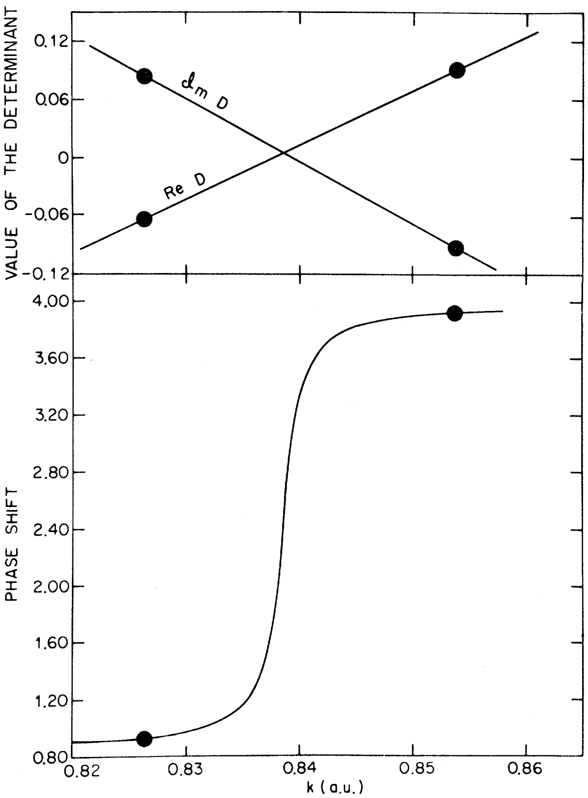

FIG. 1. Real and imaginary parts of $D(k)$ and phase shift near the lowest ^1S resonance in elastic electron–hydrogen-atom scattering. The "dots" indicate those momenta k_i where $D(k_i)$ was actually directly evaluated via the matrix methods of Sec. III A; the solid lines indicate the interpolated values.

The remaining discrepancies between the computed phase shifts and the "exact" results are probably due mainly to incompleteness in the p and d expansion basis sets. Completeness is difficult to achieve if all orbital exponents for basis functions of the same symmetry are equal since then the basis set becomes nearly redundant if more than seven or eight functions per symmetry are used; convergence is thus slowed. To obtain very high precision in the nonresonant phase shifts a more flexible basis is needed. In addition, increased flexibility is essential for a good representation of resonant scattering. This is discussed in Sec. IV B.

B. Resonance Parameters

As mentioned in Sec. III, an advantage of the present calculation is that calculation of the determinant at a few values of the energy followed by interpolation gives accurate scattering information at a continuous range of energies. The fact that this holds in the resonance region is clearly shown in Fig. 1 where interpolation of the real and imaginary parts of the determinant are shown with the phase shifts in the region near the lowest ^1S resonance. The determinant is nearly linear through the resonance region; $A[7, 7]$ interpolation gives about four significant figures in the resonance region and about six figures over the rest of the elastic region.

The resonance parameters computed with the exponent choice $\xi_s = 1.0$ are, of course, poor. This is because the rather tightly localized functions needed to represent off-resonant correlation

TABLE V. Resonance energies and widths for the lowest ^1S resonance in s-wave electron–hydrogen-atom scattering. Computations are shown in the first three angular limits for the two choices $\xi_s = 0.5$ and $\xi_s = 1.0$ which were used for all orbitals of s symmetry in the expansion.

(Basis) (Exponents)	(6, 0, 0) (1.0, -, -)	(6, 0, 0) (0.5, -, -)	(6, 8, 0) (1.0, 1.0, -)	(6, 8, 0) (0.5, 1.0, -)	(6, 8, 6) (1.0, 1.0, 1.0)	(6, 8, 6) (.5, 1.0, 1.0)	"Exact"[a]
E_{res}	-0.1068	-0.1253	-0.1413	-0.1484 a.u.	-0.1422 a.u.	-0.1484 a.u.	-0.1488
Γ_{res}	...	...	...	...	9.6×10^{-2} eV	6.8×10^{-2} eV	4.8×10^{-2} eV

[a] Resonance energy from T. F. O'Malley and S. Geltman, Ref. 3. Resonance width from P. G. Burke and A. J. Taylor, Ref. 5.

effects cannot easily describe the physically diffuse resonances[34] which are almost completely uncoupled from the background. In other words, highly accurate values of off-resonant phase shifts may be obtained from a sum [Eq. (2.2)] over pseudoresonance states which do not represent the true resonances at all[35]; for example the triplet s-wave results of Sec. IV A were accurate to almost four significant figures even though none of the pseudoresonances had energies below the first inelastic threshold.

In order to more accurately describe the lowest ^1S resonance, ξ_s was set equal to 0.5. Table IV shows convergence of the phase shifts for this exponent choice with $\xi_p = 1.0$ and $\xi_d = 1.0$. The off-resonant phase shift is nearly as good as before. Table V shows the resonance parameters obtained from a series of computations. It is clear that taking $\xi_s = 0.5$ gives a markedly improved resonance energy but only a fair value of the width.

In conclusion, it is impossible to accurately describe both resonant and nonresonant scattering with a single basis set without considerable exponent flexibility.[33,35] Nonresonant scattering, however, can be well described by a simple nonoptimized basis set.

V. DISCUSSION

The Fredholm method provides a convenient and rapid method for extracting scattering information from an optical potential. The determinant $D(E + i\epsilon)$ may be evaluated at a series of energies and easily interpolated giving scattering information over a continuous range of energies from a single major computational step. As an example of computation times, the construction of the interpolating rational fraction representation of the singlet-phase-shift below the first inelastic threshold took 30 sec for the (2, 2, 2, 2); 3.3 min for the (6, 6, 6) and 5.5 min for the (6, 8, 6) computation (times are for computation from scratch on the IBM 360-65 computer). In each case almost all of the computation time is required for calculation of matrix elements and diagonalization of H_{QQ}; once this has been done computation of $\delta(k)$ for all energies takes a negligible additional computation time. We note that extension to higher partial waves can be accomplished without introducing higher-order Bessel functions using the method of Rescigno and Reinhardt.[36]

The convergence of the results presented in Tables I–IV indicates that moderate-sized nonoptimized Slater-type basis sets provide a computationally viable method for constructing optical potentials which adequately describe nonresonant scattering. This suggests that applications to inelastic scattering and scattering from many electron atoms and ions should be computationally feasible. Accurate calculation of resonance parameters, while straightforward, will be computationally somewhat more complex.

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[27] This can be seen for the Jost function by differentiating twice Eq. (12.16) of Ref. 25 assuming an $-\alpha/2r^4$ attractive field and an appropriate nonsingular behavior at $r=0$.

[28] Reference 25, Chap. 9; M. Baker, Ann. Phys. (N. Y.) 4, 271 (1958).

[29] See, for example, the discussion of Ref. 25, p. 335.

[30] The static 2^l pole polarizability of $1s$ hydrogen in our pseudohydrogen basis is

$$\alpha^{(l)}_{\text{pseudo}} = 2 \sum_{n=l+1}^{N_l} \frac{|\langle \varphi_{10} | r^l P_l(\cos\theta) | \varphi_{nl} \rangle|^2}{\epsilon_{nl} - \epsilon_{10}},$$

where φ_{nl} is the pseudohydrogen orbital of the indicated quantum numbers, ϵ_{nl} is the associated pseudoeigenvalue, and $N_l - l$ is the number of Slater functions of l-type symmetry in the basis set. We define

$$\varphi^{(1)}_l = 2 \sum_{n=l+1}^{N_l} \frac{\langle \phi_{nl} | r^l P_l(\cos\theta) | \varphi_{10} \rangle}{\epsilon_{nl} - \epsilon_{10}} \varphi_{nl}(r)$$

the pseudo-first-order wave function. The true first-order wave function $\psi^{(l)}_1$ satisfies $(H_0 - E_{10})\psi^{(1)}_l = r^l \times P_l(\cos\theta)\psi_{10}$, where H_0 is the hydrogen-atom Hamiltonian and E_{10} and ψ_{10} are its lowest eigenvalue and eigenfunction for $\xi_s = 1.0$, $\phi_{10} = \psi_{10}$ and $\epsilon_{10} = E_{10}$. Then $\phi^{(1)}_l$ satisfies the above equation with H_0 replaced by its matrix representative in the Slater basis. But it is well known that $\psi^{(1)}_l = (a_l r^l + b_l r^{l+1})e^{-r}$ where a_l and b_l are readily determinable coefficients. Thus, if the Slater basis set contains the functions $r^l e^{-r}$ and $r^{l+1} e^{-r}$, $\phi^{(1)}_l = \psi^{(1)}_l$ and

$$\alpha^{(l)}_{\text{pseudo}} = \langle \phi_{10} | r^l P_l(\cos\theta) | \phi^{(1)}_l \rangle = \langle \psi_{10} | r^l P_l(\cos\theta) | \psi^{(1)}_l \rangle = \alpha^{(l)}_{\text{true}}.$$

But this is the case for $\xi_l = 1.0$ and $N_l - l \geq 2$. Then by the argument of Ref. 26 the optical potential will have the correct asymptotic behavior.

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[32] The notation $(n_s, n_p, n_d, \ldots)$ gives the number of Slater orbitals of each symmetry used in construction of the two-particle basis.

[33] J. J. Matese and R. S. Oberoi, Ref. 18.

[34] J. C. Y. Chen and K. T. Chung, Ref. 6(a).

[35] Conversely, if the true resonance states are used in Eq. (2.2) the sum will converge very slowly off resonance since the diffuse resonance states are weakly coupled to the $1s$ hydrogen orbital. [See Ref. 6(a)] A completely analogous situation occurs in the calculation of dynamic polarizabilities where the first-order wave function is compact in the normal dispersion region (e.g., see Ref. 30) and poorly represented by a sum over true excited states. For a good description of absorption, however, it is necessary to include diffuse functions in the basis set to properly represent the excited states.

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