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Fredholm Method. II. A Numerical Procedure for Inelastic Scattering

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A convenient and accurate numerical method is given whereby inelastic scattering information can be obtained by construction of the Fredholm determinant $\det[1-\underline{G}(E+i\epsilon)\underline{V}]$ for the coupled Lippmann-Schwinger equations. The method is noniterative and is easily applied when the potential matrix is nonlocal or energy dependent. It is shown that the determinant $\det[1-\underline{G}(E+i\epsilon)\underline{V}]$ may be factored as $\det[1-\mathcal{P}\underline{G}(E)\underline{V}]\det(1-i\underline{R})$ when $\mathcal{P}\underline{G}(E)$ is the principal-value Green's function and R is the usual R matrix of principal-value Lippmann-Schwinger theory; the R matrix may be obtained from $\det[1-\underline{G}(E+i\epsilon)\underline{V}]$ by a single partial triangularization. As a simple example of the extraction of the R matrix from the Fredholm determinant, the problem of electron scattering from hydrogen atoms is considered in the $1s$, $1s$-$2s$, $1s$-$2s$-$3s$, and $1s$-$2s$-$3s$-$4s$ close-coupling approximations. The use of optical potentials in the Fredholm theory is discussed: The two-channel problem originally suggested by Huck is solved numerically by construction of an optical potential.

I. INTRODUCTION

The fact that the S-matrix elements for many-channel potential scattering can be extracted from a single function of the channel momenta has been pointed out by LeCouteur[1]; Newton[2] has noted that this function is the Fredholm determinant for coupled many-channel Lippmann-Schwinger equations. Blankenbecler[3] has rederived these results using functional techniques; the necessary functional derivatives are evaluated using a prescription for the analytic continuation of the determinant as a function of a single complex energy. More recently, Newton[4] has given a formal extension of the method to the case of continuous channels and discussed the relation of Blankenbecler's analytic-continuation methods to the original derivation[2] based on the generalized Jost function.

Although these formal results are of great intrinsic interest, they have not been used in practical applications, except in very low orders of approximation.[3] These low-order results display the analytic properties and other qualitative features expected of the exact solutions, but certainly do not provide a computational method suitable for generating results which might be compared with experiment. It is the purpose of this paper to provide such a computational method.

In an earlier paper on one-channel scattering,[5] it was shown how a modification of Fredholm's original formal derivation of the method which bears his name provides a practical and accurate numerical scheme for the approximation of the determinant of an infinite-dimensional operator. In Sec. II, these earlier results are reviewed and the extension to many-channel scattering is presented via Newton's "substitution" rules.[2,4] It is noted that the Fredholm determinant $D(E+i\epsilon)=\det[\underline{1}-\underline{G}(E+i\epsilon)\underline{V}]$ may be factored as $\det[1-\mathcal{P}\underline{G}(E)\underline{V}]\det[\underline{1}-i\underline{R}(E)]$, where $\mathcal{P}G(E)$ denotes the principal-value Green's function, and R is the usual R matrix of principal-value Lippmann-Schwinger theory.[6] It is then shown that this factorization allows the R matrix to be extracted from $D(E+i\epsilon)$ by a single partial triangularization. Section III contains a simple example of the method in the case where the potential matrix is nonlocal and energy dependent; the problem of inelastic electron–hydrogen-atom scattering is treated in the $1s$-$2s$, $1s$-$2s$-$3s$, and $1s$-$2s$-$3s$-$4s$ close-coupling approximations. In Sec. IV the use of optical potentials is briefly discussed and a simple numerical example presented. Section V contains a summary and a conclusion.

II. FREDHOLM DETERMINANT

A. Calculation of Many-Channel Fredholm Determinant

In the case of elastic scattering from a fixed spherically symmetric potential V, which may or may not be local, all scattering information is contained in the "reference"[7] determinant

$$D(z)=\det\left(\frac{z-H}{z-H^0}\right)=\prod_l \det[1-\lambda G_l(z)V]^{(2l+1)}$$
$$=\prod_l D_l(z)^{(2l+1)}\ , \qquad (2.1)$$

where $H=H^0+\lambda V$ and the $D_l(z)$ are the "reference" determinants for the individual partial waves. $D_l(E+i\epsilon)$ is the Fredholm determinant for the partial-wave Lippmann-Schwinger equation

$$\psi_l^+(kr)=\phi_l(kr)+\lambda G_l(E+i\epsilon)V(r)\psi_l^+(kr)\ . \qquad (2.2)$$

Hereafter, we will drop the subscript l with the understanding that we are always considering one partial wave.

In I it was shown that the usual expansion

$$D(k_0)\equiv D(E+i\epsilon)=1-\lambda\int_0^\infty \frac{dE_1 V_{11}}{E+i\epsilon-E_1}$$
$$+\frac{\lambda^2}{2!}\int_0^\infty\int_0^\infty \frac{dE_1}{E+i\epsilon-E_1}\frac{dE_2}{E+i\epsilon-E_2}\begin{vmatrix} V_{11} & V_{12}\\ V_{21} & V_{22}\end{vmatrix}+$$
$$+\frac{(-\lambda)^n}{n!}\int_0^\infty\cdots\int_0^\infty \frac{dE_1\cdots dE_n}{(E+i\epsilon-E_1)\cdots(E+i\epsilon-E_n)}$$
$$\times\begin{vmatrix} V_{11} & V_{12} & \cdots & V_{1n}\\ & \cdots & & \\ V_{n1} & \cdots & & V_{nn}\end{vmatrix}+\cdots\ , \qquad (2.3)$$

with

$$V_{ij}=\langle i\,|\,V\,|\,j\rangle\equiv(2/\pi)\sqrt{k_i k_j}\int_0^\infty dr\, r^2 j_l(k_i r)V(r)j_l(k_j r), \qquad (2.4)$$

$k_i=\sqrt{2E_i}$ and $k_0=\sqrt{2E}$, could be evaluated numerically by calculation of the single (complex) determinant

$$D(k_0)=\prod_{i=1}^n\left(\frac{1}{\frac{1}{2}k_0^2-\frac{1}{2}k_i^2}\right)D'(k_0)\ , \qquad (2.5)$$

where

$$D'(k_0)\equiv\begin{vmatrix} & & & +i\pi\tilde V_{10}\\ & \underline{d}'(k_0) & & \vdots\\ & & & +i\pi\tilde V_{n0}\\ -\tilde V_{01} & \cdots & -\tilde V_{0n} & 1+i\pi\tilde V_{00}\end{vmatrix}\ . \qquad (2.6)$$

In Eq. (2.6), $d'(k_0)$ is defined by

$$d'_{ij}=(\tfrac{1}{2}k_0^2-\tfrac{1}{2}k_i^2)\,\delta_{ij}-\tilde V_{ij}\ , \quad i,j=1,2,\ldots,n \qquad (2.7a)$$

$$\tilde V_{ij}=\sqrt{k_i\omega_i}\ V_{ij}\ \sqrt{k_j\omega_j}\ , \quad i,j=0,1,2,\ldots,n \qquad (2.7b)$$

where the k_i and ω_i are the quadrature points and weights necessary to approximate integrals of the type

$$\mathcal{P}\int_0^\infty \frac{dE_1\langle k_1|V|k_1\rangle}{E-\frac{1}{2}k_1^2} \qquad (2.8a)$$

by the sum

$$\sum_{i=1}^n \frac{\omega_i k_i\langle i\,|\,V|i\rangle}{E-\frac{1}{2}k_i^2}\ . \qquad (2.8b)$$

Scattering information is extracted from $D(k_0)$ by direct calculation of the one-channel S matrix:

$$S_l(k_0)=e^{-2i\delta_l(k_0)}=\frac{D(E-i\epsilon)}{D(E+i\epsilon)}=\frac{D'(k_0)^*}{D'(k_0)}\ . \qquad (2.9)$$

The extension of these results to many-channel potential scattering is immediate: Again considering a single partial wave, we have

$$D(z)=\det[1-\lambda\underline{G}(z)\underline{V}]=\begin{vmatrix} 1-\lambda G_{11}(z)V^{11} & -\lambda G_{11}(z)V^{12} & \cdots & -\lambda G_{11}(z)V^{1\alpha} & \cdots\\ -\lambda G_{22}(z)V^{21} & 1-\lambda G_{22}(z)V^{22} & \cdots & -\lambda G_{22}(z)V^{2\alpha} & \cdots\\ & & \cdots & & \\ -\lambda G_{\alpha\alpha}(z)V^{\alpha 1} & -\lambda G_{\alpha\alpha}(z)V^{\alpha 2} & \cdots & 1-\lambda G_{\alpha\alpha}(z)V^{\alpha\alpha} & \cdots\end{vmatrix}\ , \qquad (2.10)$$

where H^0 and the unperturbed Green's functions $\underline{G}_{\alpha\alpha}(z)$ are assumed to be diagonal in the channel indices $1,2,\ldots,\alpha,\beta,\ldots$; $V^{\alpha\beta}$ is the potential matrix for the many-channel problem at hand; $V^{\alpha\beta}$ may be local, nonlocal, or even energy dependent. The many-channel analog of Eq. (2.3) is obtained by use of the identity[7]

$$\det\underline{D}(z)=\exp\mathrm{tr}\ln\underline{D}(z), \qquad (2.11)$$

which gives[8]

$$D(k_0^1, k_0^2, \ldots, k_0^\alpha, k_0^\beta, \ldots) = D(E + i\epsilon) = 1 - \lambda \sum_\alpha \int_0^\infty \frac{k_1^\alpha dk_1^\alpha V_{11}^{\alpha\alpha}}{\frac{1}{2}(k_0^\alpha)^2 + i\epsilon - \frac{1}{2}(k_1^\alpha)^2}$$

$$+ \frac{\lambda^2}{2!} \sum_{\alpha,\beta} \int_0^\infty \int_0^\infty \frac{k_1^\alpha dk_1^\alpha k_2^\beta dk_2^\beta}{[\frac{1}{2}(k_0^\alpha)^2 + i\epsilon - \frac{1}{2}(k_1^\alpha)^2][\frac{1}{2}(k_0^\beta)^2 + i\epsilon - \frac{1}{2}(k_2^\beta)^2]} \begin{vmatrix} V_{11}^{\alpha\alpha} & V_{12}^{\alpha\beta} \\ V_{21}^{\beta\alpha} & V_{22}^{\beta\beta} \end{vmatrix} + \cdots$$

$$+ (-)^n \frac{\lambda^n}{n!} \sum_{\alpha,\beta,\cdots,\eta} \int_0^\infty \frac{k_1^\alpha dk_1^\alpha k_2^\beta \cdots k_n^\eta dk_n^\eta}{[\frac{1}{2}(k_0^\alpha)^2 + i\epsilon - \frac{1}{2}(k_1^\alpha)^2] \cdots [\frac{1}{2}(k_0^\eta)^2 + i\epsilon - \frac{1}{2}(k_n^\eta)^2]} \begin{vmatrix} V_{11}^{\alpha\alpha} & V_{12}^{\alpha\beta} & \cdots & V_{1n}^{\alpha\eta} \\ V_{21}^{\beta\alpha} & V_{22}^{\beta\beta} & \cdots & \\ & \cdots & & \\ V_{n1}^{\eta\alpha} & \cdots & & V_{nn}^{\eta\eta} \end{vmatrix} + \cdots, \qquad (2.12)$$

where $k_0^\alpha = \sqrt{2(E - E_\alpha)}$, E_α being the threshold energy for the αth channel; the matrix elements are

$$V_{ij}^{\alpha\beta} = (2/\pi)\sqrt{k_i^\alpha k_j^\beta} \int_0^\infty dr\, r^2 j_l(k_i^\alpha r) V^{\alpha\beta}(r) j_l(k_j^\beta r) . \qquad (2.13)$$

The sums over channel indices are over *all* channels (open and closed), and are unrestricted.

Just as in I, the sum in Eq. (2.12) may be evaluated directly by working backwards from Fredholm's original derivation of the identity of Eq. (2.11). We introduce a numerical quadrature such that integrals of the form

$$\int_0^\infty \frac{k^\alpha dk^\alpha f(k^\alpha)}{\frac{1}{2}(k_0^\alpha)^2 + i\epsilon - \frac{1}{2}(k^\alpha)^2} = \mathcal{P} \int_0^\infty \frac{k^\alpha dk^\alpha f(k^\alpha)}{\frac{1}{2}(k_0^\alpha)^2 - \frac{1}{2}(k^\alpha)^2} - i\pi\, \mathrm{sign}(k_0^\alpha)\Theta(E - E_\alpha) f(k_0^\alpha) \qquad (2.14a)$$

are approximated by the sum

$$\sum_{i=1}^n \frac{\omega_i^\alpha k_i^\alpha f(k_i^\alpha)}{\frac{1}{2}(k_0^\alpha)^2 - \frac{1}{2}(k_i^\alpha)^2} - i\pi\, \mathrm{sign}(k_0^\alpha)\Theta(E - E_\alpha) f(k_0^\alpha) , \qquad (2.14b)$$

where k_i^α are the quadrature points and ω_i^α the appropriate weights. $\Theta(E - E_\alpha)$ is the usual step function which has been inserted to take into account the fact that the Green's function $G_{\alpha\alpha}(E)$ has no imaginary part for real energies below the threshold E_α. The function sign is defined as $\mathrm{sign}(k^\alpha) = k^\alpha / |k^\alpha|$, for real k^α. In general, a new set of quadrature points k_i^α and quadrature weights ω_i^α must be used for each open or closed channel. It may now be verified by direct expansion that if all the integrations in Eq. (2.12) are replaced by numerical quadratures of the form of Eq. (2.14b), the sum of the series may be represented as[9]

$$D(k_0^1, k_0^2, \ldots, k_0^\alpha, k_0^\beta, \ldots, k_0^\eta) = \prod_{\alpha=1}^\eta \prod_{i=1}^\eta \left(\frac{1}{\frac{1}{2}(k_0^\alpha)^2 - \frac{1}{2}(k_i^\alpha)^2} \right) D'(k_0^1, \ldots, k_0^\eta), \qquad (2.15a)$$

where

$$D'(k_0^1, k_0^2, \ldots, k_0^\alpha, k_0^\beta \ldots, k_0^\eta) = \begin{vmatrix} \underline{d}'_{11} & \cdots & \underline{d}'_{1\eta} & +i\pi \underline{\tilde{V}}_{10}^{11} + i\pi \underline{\tilde{V}}_{10}^{12} \cdots +i\pi \underline{\tilde{V}}_{10}^{1\eta} \\ & & & \cdots \\ & & & +i\pi \underline{\tilde{V}}_{n0}^{11} + i\pi \underline{\tilde{V}}_{n0}^{12} \cdots +i\pi \underline{\tilde{V}}_{n0}^{1\eta} \\ \vdots & \cdots & \vdots & \vdots \\ \underline{d}'_{\eta 1} & \cdots & \underline{d}'_{\eta\eta} & +i\pi \underline{\tilde{V}}_{10}^{\eta 1} + i\pi \underline{\tilde{V}}_{1\eta}^{\eta 2} \cdots +i\pi \underline{\tilde{V}}_{10}^{\eta\eta} \\ & & & \cdots \\ & & & +i\pi \underline{\tilde{V}}_{n0}^{\eta 1} + i\pi \underline{\tilde{V}}_{n0}^{\eta 2} \cdots +i\pi \underline{\tilde{V}}_{n0}^{\eta\eta} \\ -\tilde{V}_{01}^{11} \cdots -\tilde{V}_{0n}^{11} & \cdots & -\tilde{V}_{01}^{1\eta} \cdots -\tilde{V}_{0n}^{1\eta} & 1 + i\pi \tilde{V}_{00}^{11} + i\pi \tilde{V}_{00}^{12} \cdots +i\pi \tilde{V}_{00}^{1\eta} \\ -\tilde{V}_{01}^{21} \cdots -\tilde{V}_{0n}^{21} & \cdots & -\tilde{V}_{01}^{2\eta} \cdots -\tilde{V}_{0n}^{2\eta} & +i\pi \tilde{V}_{00}^{21} 1 + i\pi \tilde{V}_{00}^{22} \cdots \\ \cdots & \cdots & \cdots & \cdots \\ -\tilde{V}_{01}^{\eta 1} \cdots -\tilde{V}_{0n}^{\eta 1} & \cdots & -\tilde{V}_{01}^{\eta\eta} \cdots -\tilde{V}_{0n}^{\eta\eta} & +i\pi \tilde{V}_{00}^{\eta 1} \qquad \cdots 1 + i\pi \tilde{V}_{00}^{\eta\eta} \end{vmatrix} \qquad (2.15b)$$

and λ has now been set equal to 1. In Eq. (2.15b), the matrices $\underline{d}'_{\alpha\beta}$ are defined by

$$(\underline{d}'_{\alpha\beta})_{ij} = \tfrac{1}{2}[(k_0^\alpha)^2 - (k_j^\beta)^2]\delta_{ij}\delta_{\alpha\beta} - \tilde{V}_{ij}^{\alpha\beta} , \tag{2.16}$$

where

$$\tilde{V}_{ij}^{\alpha\beta} \equiv \sqrt{k_i^\alpha \omega_i^\alpha}\; V_{ij}^{\alpha\beta}\; \sqrt{k_j^\beta \omega_j^\beta} , \qquad i,j = 1,2,\ldots,n, \quad \alpha,\beta = 1,2,\ldots,\eta \tag{2.17a}$$

$$\tilde{V}_{i0}^{\alpha\beta} = (k_0^\beta)\sqrt{k_i^\alpha \omega_i^\alpha}\, V_{i0}^{\alpha\beta} \sqrt{k_0^\beta \omega_0^\beta} , \quad i = 0,1,2,\ldots,n, \quad \alpha,\beta = 1,2,\ldots,\eta \tag{2.17b}$$

$$\omega_0^\alpha = (k_0^\alpha)^{-1} .$$

Since this determinant is finite dimensional, it can be evaluated by standard numerical methods. The S-matrix elements can then be calculated using the "substitution" rules of Newton,[4] whose notation we follow:

$$S_{\alpha\alpha}(E) = \frac{D_\alpha^-(E)}{D_\alpha(E)} = \frac{D_\alpha'^-(E)}{D_\alpha'(E)} , \tag{2.18a}$$

$$[S_{\alpha\beta}(E)]^2 = \frac{D_\alpha^-(E)D_\beta^-(E) - D_{\alpha\beta}^-(E)D(E)}{[D(E)]^2} = \frac{D_\alpha'^-(E)D_\beta'^-(E) - D_{\alpha\beta}'^-(E)D'(E)}{[D'(E)]^2} , \tag{2.18b}$$

where

$$D_\alpha^-(k_0^1,k_0^2,\ldots,k_0^\alpha,\ldots,k_0^\eta) = D(k_0^1,k_0^2,\ldots,-k_0^\alpha,\ldots,k_0^\eta) , \tag{2.19a}$$

$$D_{\alpha\beta}^-(k_0^1,k_0^2,\ldots,k_0^\alpha,\ldots,k_0^\beta,\ldots,k_0^\eta) = D(k_0^1,k_0^2,\ldots,-k_0^\alpha,\ldots,-k_0^\beta,\ldots,k_0^\eta) . \tag{2.19b}$$

This direct procedure is used in Sec. IV in a simple illustration of the use of optical potentials in the Fredholm method; however, as we shall see in the following paragraph, there is a more efficient manner of extracting the S matrix from an approximate Fredholm determinant.

B. Factorization of Fredholm Determinant

Calculation of the S matrix for η open channels by direct application of the substitution rules of Eq. (2.18) involves the numerical evaluation of $\frac{1}{2}\eta(\eta+1)+1$ complex determinants. If the discrete approximation to $D(E+i\epsilon)$ involves even a moderate number of quadrature points for each channel, it is clear that for a problem involving several channels we may have to evaluate a large number of very large determinants, a rather dismal computational prospect. The first hint that this estimate of the number of determinants to be evaluated is too high is that in the case of one open channel ($\eta = 1$) we have $\frac{1}{2}\eta(\eta+1)+1 = 2$; however, in an actual calculation, only one determinant need be evaluated. This is because for one open channel

$$D(-k_\alpha) = D(k_\alpha)^* \tag{2.20a}$$

and thus

$$S_l(k_\alpha) = D(k_\alpha)^*/D(k_\alpha) . \tag{2.20b}$$

This result is generalized in the following paragraph.

The derivation hinges on the fact that[3,4]

$$\det(1 - Q\underline{A}) = \det_Q(1 - A_{QQ}) = \det(1 - \langle A_{QQ}\rangle_Q), \tag{2.21}$$

where Q is an orthogonal projector and $\det_Q$ denotes the fact that the determinant is only calculated in the subspace defined by the projector Q, $A_{QQ} = QAQ$, and $\langle A_{QQ}\rangle_Q$ denotes the matrix representation of $\underline{A}$ in the Q subspace. Consider

$$D(E+i\epsilon) = \det[1 - \underline{G}(E+i\epsilon)V] . \tag{2.22}$$

We rewrite this in terms of the principal-value Green's function

$$\mathcal{P}\underline{G}(E) \equiv \tfrac{1}{2}[\underline{G}(E+i\epsilon) + \underline{G}(E-i\epsilon)]: \tag{2.23a}$$

$$D(E+i\epsilon) = \det\{1 - [\mathcal{P}\underline{G}(E)\underline{V} - i\pi P_0(E)\underline{V}]\}, \tag{2.23b}$$

where

$$-i\pi P_0(E)V = \tfrac{1}{2}[\underline{G}(E+i\epsilon) - \underline{G}(E-i\epsilon)]$$

and $P_0(E)$ is a projector onto those eigenstates $|E_\alpha\rangle$ of H^0 which describe open channels at energy E. We have at once

$$\begin{aligned} D(E+i\epsilon) &= \det\{1 - [\mathcal{P}\underline{G}(E)\underline{V} - i\pi P_0(E)\underline{V}]\} \\ &= \det[1 - \mathcal{P}\underline{G}(E)\underline{V}]\det\left(1 + i\pi P_0(E)\underline{V}\,\frac{1}{1 - \mathcal{P}\underline{G}(E)\underline{V}}\right) \\ &= \det[1 - \mathcal{P}\underline{G}(E)\underline{V}] \\ &\quad \times \det_{P_0(E)}\left[1 + i\pi\left(V\,\frac{1}{1 - \mathcal{P}\underline{G}(E)\underline{V}}\right)P_0(E)P_0(E)\right] \\ &= \det[1 - \mathcal{P}\underline{G}(E)\underline{V}]\det[1 - i\underline{R}(E)] , \end{aligned} \tag{2.24}$$

where the matrix elements (which are numbers) of $R(E)$ are defined as

$$R_{\alpha\beta}(E) = -\pi \langle E_\alpha | \{\underline{V}[1 - \mathcal{P}\underline{G}(E)\underline{V}]^{-1}\} | E_\beta \rangle \ , \tag{2.25}$$

which is the usual definition of the R matrix.[6] We now see that

$$\frac{D^*(E+i\epsilon)}{D(E+i\epsilon)} = \frac{\det[1 - \mathcal{P}\underline{G}(E)\underline{V}]\det(1+i\underline{R})}{\det[1 - \mathcal{P}\underline{G}(E)\underline{V}]\det(1-i\underline{R})}$$

$$= \det\left(\frac{1+i\underline{R}}{1-i\underline{R}}\right) \tag{2.26}$$

and thus that

$$\frac{D^*(E+i\epsilon)}{D(E+i\epsilon)} = \det(\underline{S}) \ . \tag{2.27}$$

Equation (2.27), which was originally derived by Newton,[4] is a generalization of Eq. (2.20a). We now have the additional factorization

$$D(E+i\epsilon) = \det(1 - \mathcal{P}\underline{G}\underline{V})\det(1 - i\underline{R}) \ ,$$

which will allow direct extraction of $\underline{R}$ from $D(E+i\epsilon)$, as is shown in Sec. IIC. The advantage of this extraction is that the S matrix can be easily obtained from R by inversion of a matrix whose dimensionality is determined by the number of open channels, rather than by the number of numerical quadrature points.

C. Extraction of R Matrix from Fredholm Determinant

The R matrix may be extracted from the discrete approximation to $D(E+i\epsilon)$ by introducing a Gaussian[10] transformation which triangularizes $D'(E+i\epsilon)$, except for the last η columns. This may be seen as follows.

In a symbolic notation, we write Eq. (2.15b) as

$$D(E+i\epsilon) = \left(\prod_{\alpha=1}^{\eta}\prod_{i=1}^{n}\frac{1}{E-E_i^\alpha}\right)D'(E+i\epsilon) \tag{2.28a}$$

$$= \left(\prod_{\alpha=1}^{\eta}\prod_{i=1}^{n}\frac{1}{E-E_i^\alpha}\right)\det\begin{pmatrix} \underline{d}' & i\pi\underline{\tilde{V}} \\ -\underline{\tilde{V}}^T & 1+i\pi\underline{\tilde{V}}_0 \end{pmatrix} . \tag{2.28b}$$

In Eq. (2.28b), the dimension of the matrices $\underline{d}'$, $\underline{\tilde{V}}_0$, and $\underline{\tilde{V}}$ are $N\times N$, $\eta\times\eta$, and $\eta\times N$, respectively, where, again, η is the number of open channels[9] and N is the total number of numerical quadrature points used to construct $\underline{d}'$. Introducing a Gaussian matrix $\underline{N}^{D'}$ which triangularizes the first N columns of $\underline{D}'$, where $D'(E+i\epsilon) = \det(\underline{D}')$, we have

$$D'(E+i\epsilon) = \det(\underline{N}^{D'}\underline{D}') \tag{2.29a}$$

$$= \det\begin{pmatrix} \underline{N}^{d'}\underline{d}' & \underline{A} \\ 0 & \underline{B} \end{pmatrix} \tag{2.29b}$$

$$= \det(\underline{N}^{d'}\underline{d}')\det(\underline{B}) \ , \tag{2.29c}$$

where $\underline{N}^{d'}\underline{d}'$ is the $N\times N$ upper triangular matrix which arises directly from the complete Gaussian triangularization of the matrix $\underline{d}'$; $\underline{B}$ is a new matrix. Use has been made of the fact that the Gaussian matrix $\underline{N}^D$, which gives rise to the partial triangularization, has unit determinant.[10] The fact that the Gaussian transformation does not interchange columns implies that all scattering information is contained in the determinant of the $\eta\times\eta$ matrix $\underline{B}$, as the sign changes needed for use of the substitution rules only affect this part of $D(E+i\epsilon)$. The fact that the Gaussian transformation preserves the symmetry[11] of $\underline{D}'$ allows us to write

$$\det(\underline{B}) = \det(1 - i\underline{C}) \ , \tag{2.30}$$

$\underline{C}$ being a real symmetric $\eta\times\eta$ matrix. We now note that

$$\det[1 - \mathcal{P}\underline{G}(E)V] = \prod_{\alpha=1}^{\eta}\prod_{i=1}^{\eta}\frac{1}{E-E_i^\alpha}\det(\underline{d}') \tag{2.31a}$$

and that

$$\det(\underline{d}') = \det(\underline{N}^{d'}\underline{d}') \ . \tag{2.31b}$$

The factorization

$$D(E+i\epsilon) = \det[1 - \mathcal{P}\underline{G}(E)\underline{V}]\det(1 - i\underline{R}),$$

when combined with the results of Eqs. (2.29c) and (2.31b), allows us to conclude that $\det(1 - i\underline{R}) = \det(1 - i\underline{C})$. The fact that $\det(1 - i\underline{R})$ and $\det(1 - i\underline{C})$ contain the same scattering information[12] and the fact that the $\underline{R}$-matrix decomposition of the S matrix is unique allow us to conclude that not only are the determinants equal, but that $\underline{C} = \underline{R}$, to within irrelevant signs of the off-diagonal elements. This implies that an appropriate computational procedure is to carry out the partial triangularization of Eq. (2.29b), which may be done entirely with real arithmetic, and then to simply read off the R-matrix elements. The S matrix is then easily constructed as

$$\underline{S} = (1 + i\underline{R})/(1 - i\underline{R}) \ . \tag{2.32}$$

This result may also be obtained in a direct, if more complicated, manner by noting that if the wave functions $\psi_\alpha^P(k_0^\alpha r)$ are expanded as in Sec. III of I,[5] i.e.,

$$\psi_\alpha^P(k_0^\alpha r) = j_l(k_0^\alpha r) - \sum_i c_i^\alpha(k_i^\alpha) j_l(k_i^\alpha r) \ , \tag{2.33}$$

then the partial triangularization of Eq. (2.29b) implicitly solves the coupled principal-value Lippmann-Schwinger equations

$$\psi_\alpha^P(k_0^\alpha r) = j_l(k_0^\alpha r) + \sum_\beta \int \mathcal{P} G_{\alpha\alpha}(k_0^\alpha, r, r') \times V_{\alpha\beta}(r')\psi_\beta^P(k_0^\beta r')\, dr'$$

TABLE I. Convergence of the s-wave $1s \rightarrow 2s$ inelastic cross section [in units of $\pi(a_0)^2$] in the $1s-2s$ close-coupling approximation as a function of the number N of numerical quadrature points. The results are compared to the earlier work of Marriot[a] and Smith.[b] The energy of the incident electron is 0.5 a.u. The total computation time for calculation of σ_{12}^{+} *and* σ_{12}^{-} was 6 sec for the 33-pt calculation and 19 sec for the 66-pt calculation. In each case most of the time was taken by matrix-element calculation. The runs were carried out on a CDC 6400 computer.

		33 pts	44 pts	66 pts	88 pts	Marriot[a]	Smith[b]
Singlet	σ_{12}^{+}	0.292	0.290	0.288 28	0.288 36	0.288	0.286
Triplet	σ_{12}^{-}	0.00299	0.00295	0.002916	0.002918	0.002 74	0.0036

[a]R. Marriot, Proc. Phys. Soc. (London) 72, 121 (1958). Marriot solves the close-coupling equations by a noniterative method due to Percival, which has recently been rediscovered by Sams and Kouri [J. Chem. Phys. 51, 4809 (1969)].
[b]K. Smith, Phys. Rev. 120, 845 (1960). Smith solves the close-coupling equations by iterative solution of the integro-differential equations.

and, at the same time, constructs the R-matrix elements in such a way that the coefficients $c_i^{\alpha}(k_i^{\alpha})$ are never explicitly displayed. These coefficients may be easily obtained, if needed, by back substitution[10] from the triangularized form of the operator $[1-\mathcal{P}\underline{G}(E)\underline{V}]$, Eq. (2.31b). This alternative derivation removes the possible sign ambiguities in the off-diagonal elements of R.

III. R-MATRIX RESULTS FOR INELASTIC SCATTERING OF ELECTRONS FROM HYDROGEN

As a simple example of the method, and as a test of its numerical feasibility, calculations have been carried out for the problem of s-wave scattering of electrons from hydrogen atoms in the close-coupling approximation, with the restriction that only excitations to S states of the target are allowed. In this approximation the matrix elements of the potential are given by[13]

$$V_{ij}^{\alpha\beta} = \langle j_0(k_i^{\alpha}) \,|\, V_{\alpha\beta}(r) \pm W_{\alpha\beta} \,|\, j_0(k_j^{\beta}) \rangle$$

(+ for singlets, − for triplets), (3.1)

where

$$V_{\alpha\beta}(r) = -\frac{1}{r}\delta_{\alpha\beta} + \frac{1}{r}\int_0^r (r')^2 dr' \phi_{\alpha}(r')\phi_{\beta}(r') + \int_r^{\infty} r' dr' \phi_{\alpha}(r')\phi_{\beta}(r') \,, \quad (3.2a)$$

$$\pm\langle j_0(k_i^{\alpha}) \,|\, W_{\alpha\beta} \,|\, j_0(k_j^{\beta}) \rangle = \pm\{ (E_{\alpha} + E_{\beta} - E) \int_0^{\infty} r' dr' \times j_0(k_i^{\alpha} r')\phi_{\beta}(r') \int_0^{\infty} (r')^2 dr' j_0(k_j r')\phi_{\alpha}(r') + \int_0^{\infty} r^2 dr j_0(k_i^{\alpha} r)\phi_B(r) [(1/r) \times \int_0^r (r')^2 dr' \phi_{\alpha}(r') j_0(k_j^{\beta} r') + \int_r^{\infty} (r') dr' \phi_{\alpha}(r') j_0(k_j^{\beta} r')] \} \,, \quad (3.2b)$$

where the $\phi_{\alpha}(r)$ are the radial hydrogenic wave functions with energy E_{α}. In all the calculations reported in this section, the matrix $\underline{D}'$ was constructed as in Eq. (2.15b) and the R matrix extracted by the partial triangularization of Sec. II C. The Gaussian method with partial pivots[14] was used to carry out the triangularization. Table I shows convergence of the $1s \rightarrow 2s$ inelastic cross section as a function of the number of quadrature points for the $1s$-$2s$ calculation. Table II gives the inelastic cross sections in the $1s$, $1s$-$2s$, $1s$-$2s$-$3s$, and $1s$-$2s$-$3s$-$4s$ calculations for an electron of initial kinetic energy 0.5 a.u. incident on the ground-state target.

IV. USE OF INELASTIC OPTICAL POTENTIALS IN FREDHOLM METHOD

The numerical method described in Sec. II C becomes unwieldy for a large number of channels; this is simply because the finite-dimensional approximation to $D(E+i\epsilon)$ becomes prohibitively large. The numerical problems raised by the growth of $D(E+i\epsilon)$ are easily overcome by the use of optical potentials. This is easily seen by considering a two-channel example:

TABLE II. Cross sections for s-wave excitation of ground-state hydrogen atoms in the $1s$, $1s$-$2s$, $1s$-$2s$-$3s$, and $1s$-$2s$-$3s$-$4s$ close-coupling approximations. The incident electron has an energy of 0.5 a.u. The cross sections are given in units of $\pi(a_0)^2$, a_0 being the Bohr radius for hydrogen. Agreement with the work of K. Smith [Phys. Rev. 120, 845 (1960)] is satisfactory where comparison can be made.

Calculation	$1s$	$1s$-$2s$	$1s$-$2s$-$3s$	$1s$-$2s$-$3s$-$4s$
Singlet σ_{11}^{+}	1.07	1.13	1.23	1.25
σ_{12}^{+}	•••	0.288	0.167	0.166
σ_{13}^{+}	•••	•••	0.058	0.031
σ_{14}^{+}	•••	•••	•••	0.015
Triplet σ_{11}^{-}	3.87	3.87	3.87	3.87
σ_{12}^{-}	•••	0.0029	0.002 7	0.002 7
σ_{13}^{-}	•••	•••	0.000 066	0.000 054
σ_{14}^{-}	•••	•••	•••	0.000 003 9

$$D(E+i\epsilon) = \det\begin{pmatrix} 1-G_{11}(E+i\epsilon)V_{11} & -G_{11}(E+i\epsilon)V_{12} \\ -G_{22}(E+i\epsilon)V_{21} & 1-G_{22}(E+i\epsilon)V_{22} \end{pmatrix} . \tag{4.1}$$

Writing $G_{\alpha\alpha} \equiv G_{\alpha\alpha}(E+i\epsilon)$, this may be factored as

$$D(E+i\epsilon) = \det(1-G_{11}V_{11})\det(1-G_{22}V_{22}) \times \det\begin{pmatrix} 1 & G_{11}V_{12}/(1-G_{11}V_{11}) \\ -G_{22}V_{21}/(1-G_{22}V_{22}) & 1 \end{pmatrix} . \tag{4.2}$$

Noting that

$$\mathcal{G}_{ii} = G_{ii}/(1-G_{ii}V_{ii})$$

and that

$$\det\begin{pmatrix} \underline{I} & \underline{A} \\ \underline{B} & \underline{I} \end{pmatrix} = \det(\underline{I}-\underline{A}\underline{B}) = \det(\underline{I}-\underline{B}\underline{A}) , \tag{4.3}$$

Eq. (4.2) becomes

$$D(E+i\epsilon) = \det(1-G_{11}V_{11})\det(1-G_{22}V_{22}) \times \det(1-\mathcal{G}_{11}V_{12}\mathcal{G}_{22}V_{21}) . \tag{4.4}$$

Since Eq. (4.4) is an identity, we can use the substitution rules of Sec. II A to extract scattering information. The advantage of this form of the equation is that all the determinants have a dimensionality determined by the number of quadrature points needed to approximate *one* channel. The term $V_{12}\,\mathcal{G}_{22}V_{21}$ is known as the generalized optical potential[15] in the case that channel 2 is closed; Eq. (4.4) gives an indication of how the optical potential may be used to describe inelastic scattering when channel 2 is open. Similar results may be easily obtained for more than two channels.

As an almost trivial example of the use of inelastic optical potentials with the Fredholm method, we consider the two-channel problem originally proposed and solved by Huck.[16] The Huck potential matrix is defined by

$$\begin{aligned} V_{11} &= V_{22} = 0 , \\ V_{12} &= V_{21} = \tfrac{1}{2}c \quad \text{for } r<1 \\ &= 0 \quad \text{for } r>1 . \end{aligned} \tag{4.5}$$

The two-channel Fredholm determinant is

$$\begin{aligned} &\det\begin{pmatrix} 1 & -G_{11}V_{12} \\ -G_{22}V_{21} & 1 \end{pmatrix} \\ &= \det(1-G_{11}V_{12}G_{22}V_{21}) \\ &= \det[1-G_{11}\Sigma_{11}(E+i\epsilon)] , \end{aligned} \tag{4.6}$$

where

$$\Sigma_{11}(E+i\epsilon) = V_{12}G_{22}(E+i\epsilon)V_{21}$$

is the (complex) optical potential describing the inelasticity. The substitution rules of Sec. II A can now be used directly to evaluate the S-matrix elements, e.g.,

$$D_2^-(E) = \det[1-G_{11}(E+i\epsilon)\Sigma_{11}(E-i\epsilon)] . \tag{4.7}$$

The actual calculation proceeds exactly as in the one-channel case described in Sec. II. Results of an optical-potential calculation for the Huck model are given in Table III.

V. DISCUSSION

It has been shown that the Fredholm method provides a practical and accurate numerical procedure for constructing the S matrix for many-channel scattering problems. The principal advantage of the method is that it is easily applied when the potential matrix is nonlocal and/or energy dependent. However, it also appears that the method may be somewhat more efficient than previously existing methods in the case of low-energy electron-atom scattering. For the three-channel close-coupling calculation reported in

TABLE III. Elastic and inelastic cross sections for the Huck two-channel problem [in units of $\pi(a_0)^2$]. In each case, the numerical result is given above the exact result for the wave numbers. $k_1 = 1.0$ and $k_2 = 0.5$. For all values of c^2, 48 quadrature points were used; eight Legendre-Gauss points were used in each of the intervals $k = 0$–0.5, 0.5–1.0, 1.0–1.5, 1.5–4.0, 4.0–15.0, and 15.0–45.

$c^2 =$		2	4	6	8	10	12
σ_{11}	(numerical)	0.211 33	0.796 66	1.440 19	1.900 50	2.167 85	2.308 95
	(exact)	0.211 32	0.796 65	1.440 18	1.900 53	2.167 91	2.309 04
σ_{12}		0.389 01	0.726 23	0.866 78	0.849 46	0.767 47	0.674 34
		0.388 99	0.726 20	0.866 75	0.849 44	0.767 46	0.674 33
σ_{21}		1.556 02	2.904 92	3.467 12	3.397 84	3.069 89	2.697 36
		1.555 97	2.904 81	3.467 81	3.397 77	3.069 85	2.697 33
σ_{22}		0.249 62	0.940 81	1.700 45	2.243 51	2.558 60	2.724 59
		0.249 58	0.940 70	1.700 28	2.243 33	2.558 44	2.724 45

Sec. III, the procedure is five or six times faster than standard (noniterative) methods now in use to solve the same equations.[17] If the S matrix is desired as a function of energy, the Fredholm method is even more advantageous. Most of the time in the calculations reported here is spent in computation of the matrix elements; since a large proportion of these matrix elements do not need to be recalculated as the scattering energy is varied, the method becomes relatively more efficient for each succeeding energy. Thus, in the case that scattering information is desired over a range of energies–for example, near a resonance or threshold – it seems safe to say that the method is at least an order of magnitude faster than other methods presently in use.

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[2]R. G. Newton, J. Math. Phys. 2, 188 (1961).

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[4]R. G. Newton, J. Math. Phys. 8, 2347 (1967).

[5]W. P. Reinhardt and A. Szabo, Phys. Rev. A 1, 1162 (1970). This paper will be referred to in the text as I. I contains a brief review of previous applications of the Fredholm method to one-channel problems.

[6]See, for example, N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford U. P., London, 1965), p. 388. What we call the R matrix is often called the K matrix: See, for example, R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966), p. 190.

[7]M. Baker, Ann. Phys. (N.Y.) 4, 27 (1958). Note that in I the exponents $(2l+1)$ were inadvertently omitted from the partial-wave expansion of the full determinant.

[8]We are following the notation of Newton, Refs. 2 and 4.

[9]In order to simplify the notation we have assumed that (a) all the η channels are open, (b) in each channel the integration over momenta is approximated by an n-point numerical quadrature, and (c) the dimension of our determinant is thus $N+\eta$ when $N=n\eta$. These conventions are adopted purely for notational simplification–in an actual calculation all can be violated.

[10]J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965), Chap. 4.

[11]That is, after a symmetric matrix has been partially triangularized, the remaining portion is still symmetric.

[12]This is made clear by the realization that application of the substitution rules to $\det(1-iR)$ yields the same S-matrix elements as would be obtained by directly inverting $(1-iR)$ and constructing S as $(1+iR)\,(1-iR)^{-1}$, the only ambiguity being in the signs of off-diagonal S-matrix elements. This result gives an interesting insight into the actual mechanism of operation of the substitution rules, which otherwise seem slightly mysterious.

[13]P. G. Burke and K. Smith, Rev. Mod. Phys. 34, 458 (1962); see also S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1969), Sec. 16, for a straightforward development of these potentials.

[14]See Ref. 10. The partial pivoting is, of course, restricted to the first N rows of the determinant.

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Excitation of the $(2p^2)^3P$ State of Helium near Threshold*

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The trapped-electron method is applied to the excitation by electron impact of the $(2p^2)^3P$ state, the lowest doubly excited state of helium which is stable against auto-ionization. The energy of this state, 59.64 ± 0.08 eV, is in good agreement with theory. An estimate of the slope of the total cross section for excitation of the $(2p^2)^3P$ state at threshold gives a value of 4×10^{-20} cm^2/eV.

INTRODUCTION

Certain of the doubly excited states of helium have properties which make their observation difficult. These states, such as the $(2p^2)^3P$, $(2p3p)^1P$, and ^3P states, possess even parity but odd orbital angular momentum. They cannot be detected by a photoabsorption technique such as that used by Madden