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ALGEBRAIC VARIATIONAL METHODS IN SCATTERING THEORY*

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I. INTRODUCTION

The variational methods commonly used in scattering calculations differ in one very important respect from those commonly used in bound-state calculations. Calculations of approximate bound-state energies and the associated square-integrable wave functions are generally performed using a variational principle for the energy which provides an upper bound to the exact energy. For collision processes, however, the energy is given and the scattering parameters are to be obtained from the asymptotic part of the nonsquare-integrable wave function. The variational methods commonly used do not give rigorous upper or lower bounds to these scattering parameters. Instead the scattering variational principles are of the form that if a trial wave function is determined, then the scattering parameters can be variationally corrected to eliminate errors of first order in the inaccuracies of the trial wave function.

Algebraic variational methods are methods in which the wave function is expressed in terms of a function containing parameters and the problem is solved by obtaining the best values for the parameters. Often the function is a linear combination of predetermined basis functions. Functional variational methods are methods in which the wave function is determined without such an expansion, usually by numerically integrating the differential equations. In multidimensional problems a combination of these two techniques, such as the close-coupling method, is often used. This article is concerned with algebraic variational methods for scattering problems, but it also considers some algebraic and basis function methods which are not variationally derived.

The scattering parameters for the scattering of a particle by a central potential can all be expressed in terms of the phase shifts. These can be obtained exactly by numerical integration of a series of ordinary differential equations. This problem is called single-channel scattering. Algebraic variational methods allow the determination of scattering parameters by performing a number of one-dimensional integrals and solving a set of coupled algebraic equations. In Section II we discuss this scattering problem in detail because it affords the simplest illustrations of the techniques used in the variational methods of scattering and because it illustrates the historical development of the variational methods. It is interesting to note that the same dichotomy of numerical integration methods¹ versus algebraic methods² exists for the solution of one-dimensional bound-state problems.

For multichannel problems (scattering of a particle by a noncentral potential or scattering of composite particles), the exact solution is much more difficult. The most commonly used approximate techniques have been

perturbation theory and the close-coupling method. Generally the latter is a more accurate procedure. It involves numerical integration of a set of coupled differential or integrodifferential equations. Algebraic variational methods for this problem involve solving a set of coupled algebraic equations. In order to obtain these equations a number of multidimensional integrals must be performed. It is interesting that the same dichotomy of types of methods exists for multidimensional bound-state problems. For example, for the problem of electronic structure of atoms, the numerical Hartree-Fock method³ is an analogue of the close-coupling method and the matrix Hartree-Fock method⁴ is an algebraic variational method. As the complexities of bound-state problems increase (e.g., in going from atomic to molecular problems), the algebraic methods seem to become more and more useful as compared to numerical integration methods. It is anticipated that as algebraic variational techniques for scattering problems continue to improve, the same trend will be manifest in scattering problems also.

The oldest algebraic variational method for scattering is that developed for single-channel scattering by Hulthén⁵ in 1944. A disadvantage of the Hulthén method is that a quadratic equation must be solved. This means that, depending on the problem and the energy, either two phase shifts or nonphysical complex phase shifts may be obtained. In 1948, Kohn⁶ and Hulthén⁷ introduced new methods that do not involve nonlinear equations. In addition, Kohn explicitly showed how to apply his method to multi-channel scattering. The first application of a variational method to a problem in chemical physics was made by Huang⁸ in 1949. The method used was an extension of the work of Tamm.⁹ This method, which has been of less historical importance than the work of Hulthén and Kohn, involves the minimization of an Euler-type integral.

The methods of Hulthén and Kohn prompted a number of theoretical investigations introducing new variational methods along similar lines, clarifying the relationships between various methods, and testing the applicability of variational methods for electron-atom scattering. The most significant study was the work of Schwartz^{10,11} in 1961. Using the Kohn procedure he found that the calculations of the phase shifts are plagued by nonphysical singularities. These singularities, which are just artifacts of the Kohn method, show the phase shift increases (or decreases) rapidly by π radians as a function of energy. In other words, the Kohn method predicts a resonance or antiresonance where no physical structure should exist. Schwartz also found that as the basis set is increased in size the number of singularities increases, but the widths of the spurious structures become narrower. This suggests that as the trial wave function approaches the exact wave function these singularities become

undetectable. Nevertheless, they provide serious problems in practical applications of the Kohn method. Thus the work of Schwartz uncovered a disappointing feature of the use of the Kohn method.

Harris¹² stimulated renewed interest in algebraic scattering calculations by proposing in 1967 an algebraic method that could easily be used for single-channel scattering calculations. The Harris method can be used only at certain energies determined by the basis set, but the basis set can be adjusted to make one of these energies equal to the energy of interest. Nesbet,¹³ in a critical evaluation of the Hulthén, Kohn, and Harris methods, presented the first correct analysis of the source of spurious singularities in Kohn method calculations, suggested a method (the anomaly-free method) for avoiding these spurious singularities, and clarified the relation between the Harris method and the variational methods. In another important contribution, Nesbet¹⁴ clearly and explicitly extended the Kohn method and the anomaly-free method to multi-channel scattering.

Harris and Michels^{15,16} modified the Harris method for single-channel scattering so it is variational and can be used at any energy. They also extended the modified method (called the minimum-norm method) to inelastic scattering and reviewed¹⁶ all previous work. References to the work done in the period from 1967 to 1971 also have been summarized elsewhere.¹⁷⁻¹⁹

Recently there have been many new important ideas and these (along with a fuller discussion of the material briefly reviewed above) are discussed in subsequent sections. The present outlook for algebraic variational methods in scattering is very promising but actual applications of the ideas that have been developed have still barely scratched the surface. Further, applications in chemical physics have been restricted almost entirely to electron-atom collisions.

Since scattering problems not involving explicitly time-dependent fields can always be solved by time-independent quantum mechanics, and since doing so is usually more convenient than using time-dependent quantum mechanics, we restrict our attention to time-independent formulations in this article.

Section II involves the application of algebraic variational methods to single-channel scattering problems. We use the *s*-wave scattering of a particle with the mass of an electron off an attractive exponential as an illustrative example. Another example of single-channel scattering is the scattering of electrons by atoms in the static approximation.^{20,21} In the static approximation, one approximates the wave function as a ground state atomic wave function times a nonsquare-integrable function of the scattering electron's coordinates. In this way the problem reduces to a

particle scattering off a central potential. The inclusion of electron exchange into the calculation by antisymmetrizing the wave function in the coordinates of all the electrons results in an additional potential term which is nonlocal. This is called the static exchange approximation (or often just the exchange approximation).^{21,22} We defer discussion of the exchange approximation and other treatments of electron-atom scattering which go beyond the static approximation to Section III.

Since the phase shifts in the single-channel case can be obtained to any desired accuracy by numerical integration of the ordinary differential equation (not a difficult computational task), the motivation of considering algebraic variational methods in that case is to learn more about them so they can be applied most advantageously to multichannel cases. Multichannel cases are considered explicitly in Section III.

II. SINGLE-CHANNEL SCATTERING

A. Wave Functions

Consider the scattering of a particle off a potential $V(r)$, where r is the coordinate of the particle with respect to the origin. The wave function $\psi(r)$ must satisfy the Schrödinger equation

$$(H - E)\psi(r) = 0 \quad (1)$$

where H is the Hamiltonian operator, and E is the total energy of the system. For collision problems the total energy is given, and the asymptotic part of the wave function is to be determined. If the wave function is expanded in partial waves

$$\psi(r) = \sum_l \frac{X_l(r)}{r} P_l(\cos \theta) \quad (2)$$

where $P_l(\cos \theta)$ is the Legendre polynomial of order l ; the function $X_l(r)$ is the solution to²³

$$L_l X_l = 0 \quad (3)$$

where the operator L_l is defined as

$$L_l = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) - E \quad (4)$$

with the boundary condition

$$X_l(0) = 0 \quad (5)$$

The solutions of (4) with $V(r) = 0$ are r times the spherical Bessel (j_l) and Neumann ($-y_l$) functions. They are characterized by the boundary

conditions²⁴

$$krj_l(kr) \underset{r \rightarrow \infty}{\sim} \sin(kr - \frac{1}{2}l\pi) \quad (6a)$$

$$kr\xi_l(kr) \underset{r \rightarrow \infty}{\sim} \cos(kr - \frac{1}{2}l\pi) \quad (6b)$$

$$j_l(kr) \underset{r \rightarrow 0}{\sim} \frac{(kr)^l}{(2l+1)!!} \quad (6c)$$

and

$$\xi_l(kr) \underset{r \rightarrow 0}{\sim} \frac{(2l-1)!!}{(kr)^{l+1}} \quad (6d)$$

The wave number vector \mathbf{k} is related to the energy by

$$E = \frac{\hbar^2 k^2}{2m} \quad (7)$$

For potentials of shorter range than a coulomb potential the solution of (3) is asymptotically equal to some linear combination of $rj_l(kr)$ and $r\xi_l(kr)$. If we force the coefficient of $\sin(kr - \frac{1}{2}l\pi)$ to be unity, we have

$$X_l(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} kr [j_l(kr) + t_l \xi_l(kr)] \quad (8)$$

where a_0 is a unit of length (taken to be the bohr in numerical examples) and t_l is the tangent of the partial wave phase shift η_l . The problem is the calculation of η_l and the solution of (3) subject to the boundary conditions (5) and (8). The partial cross-sections σ_l are related to the partial wave phase shifts by

$$\sigma_l = \left(\frac{4\pi}{k^2}\right) (2l+1) \sin^2 \eta_l \quad (9)$$

The total cross-section is

$$Q = \sum_l \sigma_l \quad (10)$$

The total cross-section may also be written

$$Q = 2\pi \int d\theta |f(\theta)|^2 \quad (11)$$

in terms of the scattering amplitude. The scattering amplitude is related to the phase shifts by

$$f(\theta) = \frac{1}{2ik} \sum_l (2l+1) (e^{2i\eta_l} - 1) P_l(\cos \theta) \quad (12)$$

We shall consider the problem of determining $X_l(r)$ and t_l . Methods exist for the determination of $\psi(r)$ and $f(\theta)$ without making the expansion

(2) but they are generally less useful for accurate work and we do not consider them here.

B. The Variational Expressions

Consider the functional^{25,26}

$$I_i(X_i^0) = \int_0^\infty X_i^0(r) L_i X_i^0(r) dr \quad (13)$$

where X_i^0 is a trial radial wave function satisfying

$$X_i^0(0) = 0 \quad (14)$$

$$X_i^0(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r [j_i(kr) + t_i^0 \xi_i(kr)] \quad (15)$$

where $t_i^0 = \tan \eta_i^0$. The trial radial wave function can be written

$$X_i^0(r) = X_i(r) + \delta X_i(r) \quad (16)$$

where $X_i(r)$ is the solution of (3). Then

$$\delta X_i(0) = 0 \quad (17)$$

$$\delta X_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r \xi_i(kr) \delta t_i \quad (18)$$

where

$$\delta t_i = t_i^0 - t_i \quad (19)$$

We assume $V(r)$ is real so that $X_i^0(r)$, $X_i(r)$, and $\delta X_i(r)$ are real. We can express the error in I_i as

$$\delta I_i = I_i(X_i^0) - I_i(X_i) \quad (20)$$

where the last term is zero. Using (16) this becomes

$$\delta I_i \cong \int_0^\infty dr X_i(r) L_i \delta X_i(r) \quad (21)$$

where we have neglected terms that are of order $(\delta X_i)^2$. Using (3) and (4), (21) becomes

$$\delta I_i \cong - \left(\frac{\hbar^2}{2m} \right) \int_0^\infty dr \left(X_i \frac{d^2}{dr^2} \delta X_i - \delta X_i \frac{d^2}{dr^2} X_i \right) \quad (22a)$$

$$\cong - \frac{\hbar^2}{2m} \left[X_i \frac{d}{dr} \delta X_i - \delta X_i \frac{d}{dr} X_i \right]_0^\infty \quad (22b)$$

Using (5), (6), (8), (17), and (18), (22b) becomes

$$\delta I_i \cong \left(\frac{\hbar^2}{2ma_0} \right) k \delta t_i \quad (23)$$

Thus the expression

$$t_i^K = t_i^0 - \left(\frac{2ma_0}{\hbar^2 k} \right) I_i(X_i^0) \quad (24)$$

is a stationary expression for the tangent of the phase shift; that is, the first-order correction to the variationally corrected quantity t_i^K vanishes by (23). An expression equivalent to (24) was first derived by Hulthén⁵ and (24) may be called Hulthén's variational expression. Equation (24) is also used in Kohn's variational method⁶ and because of this it will be called Kohn's variational expression.²⁶ To complete the specification of the variational methods²⁶ requires giving procedures to determine t_i^0 and $X_i^0(r)$, which are needed to evaluate the right-hand side of (24).

Hulthén's second method⁷ can be reformulated²⁷ using a variational expression for the cotangent of the phase shift. This expression may be derived as above except using the normalizations

$$X_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r [t_i^{-1} j_i(kr) + \xi_i(kr)] \quad (25)$$

$$X_i^0(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r [(t_i^0)^{-1} j_i(kr) + \xi_i(kr)] \quad (26)$$

Then we obtain the following stationary expression for the cotangent of the phase shift

$$(t_i^R)^{-1} = (t_i^0)^{-1} + \left(\frac{2ma_0}{\hbar^2 k} \right) I_i(X_i^0) \quad (27)$$

Note that $X_i^0(r)$ in (27) is normalized according to (26). If we wish to use $X_i^0(r)$ normalized according to (15) we must use

$$(t_i^R)^{-1} = (t_i^0)^{-1} + \left[\frac{2ma_0}{\hbar^2 k (t_i^0)^2} \right] I_i(X_i^0) \quad (28)$$

(27) or (28) can be called the variational expression of the second Hulthén method or the inverse Kohn variational expression. Moiseiwitsch and Stacey^{9,47} and Williams²⁸ have shown that Hulthén's second method is equivalent to the method derived later by Rubinow.^{29,30} To avoid ambiguity we use the symbol R (for Rubinow) for this variational expression.

A more general expression was derived by Kato for s -waves.³¹ Generalizing to arbitrary l we consider

$$X_l(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r [\lambda_{\theta,l} j_l(kr + \theta) + \xi_l(kr + \theta)] \quad (29)$$

$$X_l^0(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r [\lambda_{\theta,l}^0 j_l(kr + \theta) + \xi_l(kr + \theta)] \quad (30)$$

where θ is an arbitrary constant. Note

$$\lambda_{\theta,l} = [\tan(\eta_l - \theta)]^{-1} \quad (31)$$

Then we obtain the following stationary expression for $\lambda_{\theta,l}$

$$\lambda_{\theta,l}^{\text{Kato}} = \lambda_{\theta,l}^0 + \frac{2ma_0}{\hbar^2 k} I(X_l^0) \quad (32)$$

Note that $X_l^0(r)$ in (32) is normalized as in (30). Kato³¹ also derived an explicit expression for the error in (32). This result may be stated in the form of the following equation for the exact $\lambda_{\theta,l}$:

$$\lambda_{\theta,l} = \lambda_{\theta,l}^0 + \frac{2ma_0}{\hbar^2 k} [I(X_l^0) - I(\delta X_l)] \quad (33)$$

which is called the Kato identity.

Percival³² suggested using an alternative form of (24). He used the normalizations

$$X_l^0(r) \underset{r \rightarrow \infty}{\sim} kr[\alpha_{0l}^0 j_l(kr) + \alpha_{1l}^0 \xi_l(kr)] \quad (34)$$

and

$$\begin{aligned} \delta X_l(r) \underset{r \rightarrow \infty}{\sim} [Q \cos(\eta_l^0 + \delta\eta_l) - \alpha_{0l}^0] kr j_l(kr) \\ + [Q \sin(\eta_l^0 + \delta\eta_l) - \alpha_{1l}^0] kr \xi_l(kr) \end{aligned} \quad (35)$$

where

$$\alpha_{0l}^0 = Q \cos \eta_l^0 \quad (36a)$$

and

$$\alpha_{1l}^0 = Q \sin \eta_l^0 \quad (36b)$$

to obtain the stationary expression for the phase shift given by

$$\eta_l^P = \eta_l^0 - \frac{2m}{\hbar^2 k |Q|^2} I(X_l^0) \quad (37)$$

Note that $X_l^0(r)$ in (37) is normalized according to (34) and (36). If we wish to use $X_l^0(r)$ normalized according to (15) we must use

$$\eta_l^P = \eta_l^0 - \frac{2ma_0}{\hbar^2 k} \cos^2 \eta_l^0 I(X_l^0) \quad (38)$$

Seaton³³ showed that (37) can also be obtained starting from

$$\delta X_l(r) \underset{r \rightarrow \infty}{\sim} [-\alpha_{1l}^0 j_l(kr) + \alpha_{0l}^0 \xi_l(kr)] kr \delta\eta_l \quad (39)$$

(35) and (39) are identical through first order in $\delta\eta_l$.

Above we have given variationally correct expressions for t_l , t_l^{-1} , $[\tan(\eta_l - \theta)]^{-1}$, and η_l . Variationally correct expressions may be derived for other functions of η_l but they have been of less interest.

C. The Hulthén, Kohn, Rubinow, and Percival Methods

For basis set calculations, the trial radial wave function $X_i^0(r)$ is written as the following linear combination

$$X_i^0(r) = S_i(r) + t_i^0 C_i(r) + \sum_{a=1}^n c_a^i \eta_a^i(r) \quad (40)$$

where

$$S_i(0) = 0 \quad (41)$$

$$C_i(0) = 0 \quad (42)$$

$$S_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r j_i(kr) \quad (43)$$

$$C_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r \xi_i(kr) \quad (44)$$

the $\eta_a^i(r)$ are a set of square-integrable functions, and the c_a^i and t_i^0 are $(n+1)$ coefficients to be determined. To satisfy (5) we require

$$\eta_a^i(0) = 0 \quad (45)$$

Note that (8) is automatically satisfied by $X_i^0(r)$ of (40).

The Kohn variational method^{6,26} for obtaining the $(n+1)$ coefficients in the trial function consists in solving the $(n+1)$ equations

$$\frac{\partial t_i^K}{\partial c_a^i} = 0 \quad a = 1, 2, \dots, n \quad (46)$$

$$\frac{\partial t_i^K}{\partial t_i^0} = 0 \quad (47)$$

Equation (46) may be written

$$\int_0^\infty dr \eta_a^i(r) L_i X_i^0(r) = 0 \quad a = 1, 2, \dots, n \quad (48)$$

and (47) may be written

$$\int_0^\infty dr C_i(r) L_i X_i^0(r) = 0 \quad (49)$$

[The latter is derived by using (70).] The trial t_i^0 obtained by this procedure will be called the Kohn zero-order result t_{K^0} , where we have dropped the subscript l .

The Hulthén variational method⁵ for the $(n+1)$ coefficients in the trial function consists in solving (46) [or the equivalent (48)] and

$$I(X_i^0) = 0 \quad (50a)$$

Equation (50a) has two solutions (discussed later). One of these is called the Hulthén zero-order result t_H^0 . Equation (50a) may be written [using (48)]

$$\int_0^\infty dr[S_i(r) + t_i^0 C_i(r)]L_i X_i^0(r) = 0 \quad (50b)$$

We have already mentioned that the second Hulthén⁷ and Rubinow methods^{29,30} are identical. They yield a t_i^0 which will be called the Rubinow zero-order result t_R^0 . To obtain the t_R^0 , we use the trial function

$$X_i^0(r) = (t_i^0)^{-1} S_i(r) + C_i(r) + \sum_{a=1}^n c_a^i \eta_a^i(r) \quad (51)$$

and solve the equations

$$\frac{\partial (t_i^R)^{-1}}{\partial c_a^i} = 0 \quad a = 1, 2, \dots, n \quad (52)$$

$$\frac{\partial (t_i^R)^{-1}}{\partial (t_i^0)^{-1}} = 0 \quad (53)$$

for the $(n+1)$ coefficients in (51). Equation (52) may be written as (48), and (53) may be written

$$\int_0^\infty dr S_i(r) L_i X_i^0(r) = 0 \quad (54)$$

These procedures yield variationally uncorrected tangents of the phase shift which may be improved (or corrected through first order, i.e., corrected to second order³⁰) by using (24), (28), or (38). Usually t_K^0 is corrected to give t_K^K by (24) and t_R^0 is corrected to give t_R^R by (28) because^{13,16} the corrected tangents are then stationary with respect to the zero-order tangents, that is,

$$\left. \frac{\partial t_i^K}{\partial t_i^0} \right|_{t_i^0 = t_i^K} = 0 \quad (55)$$

and

$$\left. \frac{\partial t_i^R}{\partial t_i^0} \right|_{t_i^0 = t_i^R} = 0 \quad (56)$$

The properties (55) and (56) are discussed later in this section. Kohn zero-order tangents may be corrected by the Rubinow variational expression to give nonstationary t_K^R or by the Percival expression to give t_K^P , or the Rubinow zero-order tangents may be corrected by the Kohn variational expression to give the nonstationary t_R^K . The nonstationary quantity t_R^P may also be obtained, but it is not considered in this article.

Hulthén's variational method obviously yields a trial wave function for which the variational correction computed by (24), (28), or (38) vanishes. Thus

$$t_H^0 = t_H^K = t_H^R = t_H^P \quad (57)$$

and this quantity may simply be called the Hulthén tangent t_H .

Percival's variational expression²² uses the trial function

$$X_i^0(r) = a_0^{-1/2} [\cos \eta_i^0 S_i(r) + \sin \eta_i^0 C_i(r)] + \sum_{a=1}^n c_a^i \eta_a^i \quad (58)$$

The $(n+1)$ unknowns in (58) are obtained by solving the $(n+1)$ equations

$$\frac{\partial \eta_i^P}{\partial c_a^i} = 0 \quad a = 1, 2, \dots, n \quad (59)$$

$$\frac{\partial \eta_i^P}{\partial \eta_i^0} = 0 \quad (60)$$

Equation (59) may be written as (48), and (60) is a transcendental equation for η_P^0 which can be rewritten as a quadratic equation for $\tan 2\eta_P^0$. The zero-order Percival result η_P^0 obtained this way is variationally corrected using (38) to yield η_P^P .

The methods explained above can be rederived in a fashion that yields equations more suitable for subsequent discussion. For this purpose we present the following analysis due to Nesbet.¹³ We expand the radial wave function in a form slightly different from (40), namely,

$$X_i^0 = \phi_0^i(r) + S_i(r) + t_i^0 [\phi_1^i(r) + C_i(r)] \quad (61)$$

where

$$\phi_0^i = \sum_{a=1}^n c_a^{S_i} \eta_a^i(r) \quad (62)$$

and

$$\phi_1^i = \sum_{a=1}^n c_a^{C_i} \eta_a^i(r) \quad (63)$$

Equations (48) are replaced by the equations

$$\int_0^\infty dr \eta_a^i(r) L_i \phi_0^i(r) = - \int_0^\infty dr \eta_a^i(r) L_i S_i(r) \quad a = 1, 2, \dots, n \quad (64)$$

and

$$\int_0^\infty dr \eta_a^i(r) L_i \phi_1^i = - \int_0^\infty dr \eta_a^i(r) L_i C_i(r) \quad a = 1, 2, \dots, n \quad (65)$$

From (13), (61), (64), and (65) we obtain

$$I(X_i^0) = M^{00} + (M^{01} + M^{10}) t_i^0 + (M^{11}) (t_i^0)^2 \quad (66)$$

where

$$M^{\alpha\beta} = \int_0^{\infty} dr A_{i\alpha}(r) L_{i\beta}[\phi_{\beta}^l(r) + A_{i\beta}(r)] \quad \alpha, \beta = 0, 1 \quad (67)$$

and we have the following new labels

$$A_{i0}(r) = S_i(r) \quad (68)$$

$$A_{i1}(r) = C_i(r) \quad (69)$$

where we have suppressed the pair of subscripts l which could have been added to the $M^{\alpha\beta}$'s. Note an important property of these matrix elements:

$$M^{01} - M^{10} = \frac{\hbar^2 k}{2ma_0} \quad (70)$$

which can be derived by integration-by-parts and evaluation of the resulting surface integral.

Now equations (50), (47), (53), and (60) can be written in the present notation as

$$M^{00} + (M^{01} + M^{10})t_H + M^{11}t_H^2 = 0 \quad (71)$$

$$M^{10} + M^{11}t_K^0 = 0 \quad (72)$$

$$M^{00} + M^{01}t_R^0 = 0 \quad (73)$$

and

$$\frac{\hbar^2 k}{2ma_0} - (M^{11} - M^{00}) \sin 2\eta_P^0 - (M^{01} + M^{10}) \cos 2\eta_P^0 = 0 \quad (74)$$

respectively.

The Hulthén tangent of the phase shift is given by the solution of the quadratic equation (71). At one time the fact that two phase shifts are obtained this way was considered a problem. It has been shown, however, that the physical solution, if any, is obtained with the positive sign³⁴⁻³⁶ of the discriminant, giving

$$t_H = -\frac{M^{10}}{M^{11}} + \frac{\hbar^2 k}{4ma_0 M^{11}} \left\{ \left[-16 \left(\frac{ma_0}{\hbar^2 k} \right)^2 \text{DET } M + 1 \right]^{1/2} - 1 \right\} \quad (75)$$

where we have used capital letters for a determinant of a matrix arranged by its superscripts, that is,

$$\text{DET } M = M^{00}M^{11} - M^{10}M^{01} \quad (76)$$

From (75) it is easily seen that t_H is complex if

$$\text{DET } M > \frac{(\hbar^2 k / ma_0)^2}{16} \quad (77)$$

In this case there is no physical solution of (71).

The zero-order Kohn and Rubinow phase shifts given by (72) and (73), that is,

$$\eta_K^0 = \arctan \left(\frac{-M^{10}}{M^{11}} \right) \quad (78)$$

$$\eta_R^0 = \arctan \left(\frac{-M^{00}}{M^{01}} \right) \quad (79)$$

can be corrected through first order using the Kohn variational expression (24), the Rubinow variational expression (28), or the Percival variational expression (38). Using (70) these procedures yield

$$t_K^K = -\frac{M^{10}}{M^{11}} - \frac{2ma_0}{\hbar^2 k} \frac{\text{DET } M}{M^{11}} \quad (80a)$$

$$= -\frac{2ma_0}{\hbar^2 k} \left[M^{00} - \frac{(M^{10})^2}{M^{11}} \right] \quad (80b)$$

$$t_R^K = -\frac{M^{00}}{M^{01}} - \frac{2ma_0}{\hbar^2 k} \frac{M^{00} \text{DET } M}{(M^{01})^2} \quad (81)$$

$$(t_K^R)^{-1} = -\frac{M^{11}}{M^{10}} + \frac{2ma_0}{\hbar^2 k} \frac{M^{11} \text{DET } M}{(M^{10})^2} \quad (82)$$

$$(t_R^R)^{-1} = -\frac{M^{01}}{M^{00}} + \frac{2ma_0}{\hbar^2 k} \frac{\text{DET } M}{M^{00}} \quad (83)$$

and

$$t_K^P = \tan \left[-\arctan \frac{M^{10}}{M^{11}} - \frac{2ma_0}{\hbar^2 k} \cos^2 \eta_K^0 \frac{\text{DET } M}{M^{11}} \right] \quad (84)$$

We now consider the properties (55) and (56). From (24) and (66) we have

$$t^K = t^0 - \frac{2ma_0}{\hbar^2 k} [M^{00} + (M^{01} + M^{10})t^0 + M^{11}(t^0)^2] \quad (85)$$

Differentiating

$$\frac{\partial t^K}{\partial t^0} = 1 - \frac{2ma_0}{\hbar^2 k} [M^{01} + M^{10} + 2M^{11}t^0] \quad (86)$$

Substituting $t^0 = t_K^0$ [from (78)] and using (70) yields (55). That this must occur was ensured by using (47) to define t_K^0 . Thus t_K^K is not only correct through first order but is also stationary with respect to variations of the zero-order tangent of the phase shift. A similar argument shows $(\partial t^K / \partial t^0)|_{t^0=t_R^0}$ is not zero. Thus the Kohn variational expression is stationary with respect to t^0 only if the Kohn method is used to obtain t^0 . As a consequence, although t_R^K is correct through first order, it is not stationary with respect to variations in the zero-order tangent of the phase shift.

Similarly we can show that t_R^R and t_P^P are stationary but t_K^R and t_K^P are not. The variationally correct and stationary results t_K^K and t_R^R are, as mentioned previously, the Kohn and Rubinow first-order results, respectively. The methods yielding t_P^P and t_K^P were used by Percival,³² but the other two methods (yielding t_R^K and t_K^R) do not appear to have been used in the literature.

Many examples of potential scattering calculations using the Hulthén, Kohn, and Rubinow methods may be found in the literature.^{5-7,13,29,34-36,37-47} Applications to more complicated problems are discussed in Section III.

Notice from (75), (76), and (78) to (84) that when $\text{DET } M$ is 0 we have

$$t_K^0 = t_R^0 = t_H = t_K^K = t_R^R = t_R^K = t_K^R = t_K^P \quad (87)$$

For single-channel scattering the reactance matrix is a 1×1 matrix whose element is t_l . Thus we have been considering special cases of variational methods for the reactance matrix. Analogous variational methods of the types considered here and below may be written down for the scattering matrix.⁶ For single-channel problems the scattering matrix is a 1×1 matrix whose element is $e^{2i\eta_l}$. Thus these methods may yield complex η_l . Further, they are often less convenient since they require use of complex asymptotic functions in place of S_l and C_l . Thus we do not consider them explicitly.

D. Integrals and Computational Procedures

Note that the calculations discussed in the last section reduce to the computation of the various $M^{a\beta}$. Nesbet¹³ has given expressions for the $M^{a\beta}$ in terms of the set of basis functions

$$\bar{\eta}_v^i = \sum_{a=1}^N c_a^{iv} \eta_a^i(r) \quad (88)$$

where the c_a^{iv} are obtained by solving the standard eigenvalue problem

$$\sum_b H_{ab}^i c_b^{iv} = E_v^i c_a^{iv}, \quad a = 1, 2, \dots, n \quad (89)$$

$$v = 1, 2, \dots, n$$

where

$$H_{ab}^i = \int_0^\infty dr \eta_a^i(r) (L_i + E) \eta_b^i(r) \quad (90)$$

These expressions are

$$M^{00} = M_{SS} + \sum_v M_{Sv} (E - E_v)^{-1} M_{vS} \quad (91)$$

$$M^{01} = M_{SC} + \sum_v M_{Sv} (E - E_v)^{-1} M_{vC} \quad (92)$$

$$M^{10} = M_{CS} + \sum_v M_{Cv} (E - E_v)^{-1} M_{vS} \quad (93)$$

and

$$M^{11} = M_{CC} + \sum_{\nu} M_{C\nu}(E - E_{\nu})^{-1}M_{\nu C} \quad (94)$$

where

$$M_{SS} = \int_0^{\infty} dr S_i(r) L_i S_i(r) \quad (95)$$

$$M_{SC} = \int_0^{\infty} dr S_i(r) L_i C_i(r) \quad (96)$$

$$M_{CS} = \int_0^{\infty} dr C_i(r) L_i S_i(r) \quad (97)$$

$$M_{CC} = \int_0^{\infty} dr C_i(r) L_i C_i(r) \quad (98)$$

and

$$M_{\nu C} = M_{C\nu} = \int_0^{\infty} dr C_i(r) L_i \tilde{\eta}_{\nu}^i(r) \quad (99)$$

$$M_{\nu S} = M_{S\nu} = \int_0^{\infty} dr S_i(r) L_i \tilde{\eta}_{\nu}^i(r) \quad (100)$$

Alternative expressions for the $M^{\alpha\beta}$ can be obtained which do not require the solution of (89). For these expressions we assume

$$\int_0^{\infty} dr \eta_a^i(r) \eta_b^i(r) = \delta_{ab} \quad (101)$$

and

$$\int_0^{\infty} dr A_{i\beta}(r) \eta_a^i(r) = 0 \quad (102)$$

Then¹⁶

$$M^{\alpha\beta} = (M^{AA} - M^{A\eta} M^{\eta\eta^{-1}} M^{\eta A})_{\alpha\beta} \quad (103)$$

where

$$M_{ab}^{\eta\eta} = \int_0^{\infty} dr \eta_a^i(r) L_i \eta_b^i(r) \quad (104)$$

$$M_{\alpha\beta}^{AA} = \int_0^{\infty} dr A_{i\alpha}(r) L_i A_{i\beta}(r) \quad \alpha, \beta = 0, 1 \quad (105)$$

$$M_{\alpha\beta}^{\eta A} = \int_0^{\infty} dr \eta_a^i(r) L_i A_{i\beta}(r) \quad \beta = 0, 1 \quad (106)$$

$$M_{\beta\alpha}^{A\eta} = \int_0^{\infty} dr A_{i\beta}(r) L_i \eta_a^i(r) \quad \beta = 0, 1 \quad (107)$$

Note that (101) and (102) are not really needed to derive (103), as was assumed by previous workers. This is discussed in Appendix 1.

The integrals (90) and (104) are called bound-bound integrals, the integrals (99), (100), (106), and (107) are called bound-free integrals, and the integrals (95) to (98) and (105) are called free-free integrals.

Equations (91) to (94) have the advantage over equation (103) that if (89) is once solved, scattering calculations may be performed at many energies E by simply doing the new free-free integrals (95) to (98) and bound-free integrals (99) and (100). Using (103), however, we must invert M^{nn} at each new energy.

E. The Harris Method (for Energies Equal to Eigenvalues of the Bound-Bound Matrix)

Harris¹² pointed out a simple method for calculating the tangent of the phase shift in the case where the energy is equal to one of the eigenvalues E_μ^i of the bound-bound matrix. In this case, if we write the trial function as

$$X_i^0(r) = S_i(r) + t_i^0 C_i(r) + \sum_\nu d_\nu \tilde{\eta}_\nu^i(r) \quad (108)$$

involving the expansion coefficients d_ν and require $L_i X_i^0(r)$ to have no component in the space spanned by the η_a^i we obtain

$$t_{\text{Harris}} = \frac{-\int_0^\infty dr \tilde{\eta}_\mu^i(r) L_i S_i(r)}{\int_0^\infty dr \tilde{\eta}_\mu^i(r) L_i C_i(r)} \quad (109)$$

Nesbet¹³ showed that when E equals one of the eigenvalues E_μ^i

$$t_{\text{Harris}} = t_R^0 = t_K^0 = t_H \quad (110)$$

However, the Harris method has the advantage over the previous methods that no free-free integrals need to be evaluated.

A possible difficulty with the Harris method is that the basis set has to be adjusted to perform a calculation at a preselected energy. If such basis set adjustment were required to calculate the phase shift as a function of energy in some energy region, spurious energy dependences of the phase shifts could be obtained. This is not expected to be a problem if large enough basis sets are used. Another disadvantage¹⁸ however is that, because the eigenvalue E_μ^i depends on the trial function, the extrapolation technique as basis functions approach a complete set cannot be used.

Formally a more serious difficulty with the Harris method is that the tangent of the phase shift is not variationally corrected. When the

minimum-norm method of Harris and Michels (discussed in the next section) is applied at an energy equal to one of the eigenvalues E_{μ}^i , it reduces to the Harris method but with the addition of a variational correction. For this reason t_{Harris} may be called t_{MN}^0 .

Some applications of the original Harris method to potential scattering may be found in the literature.^{12,13,44,45}

F. The Minimum-Norm Method

Harris and Michels¹⁵ derived an extension of the Harris method called the minimum-norm method which can be applied at any incident energy with any basis set. The radial wave function is expanded in the form

$$X_i^0(r) = \sum_{\beta=0}^1 \alpha_{\beta i}^0 A_{i\beta}(r) + \sum_{a=1}^n c_a^i \eta_a^i(r) \quad (111)$$

where the $\alpha_{\beta i}^0$ and c_a^i are coefficients. We must first determine t_{MN}^0 , the zero-order minimum-norm tangent of the phase shift, given by

$$\tan \eta_i^0 = \frac{\alpha_{1i}^0}{\alpha_{0i}^0} \quad (112)$$

We consider a region defined as $0 \leq r \leq a$ where a is large enough so that the integrals (101), (102), and (104) to (107) would all be approximately unchanged if the integration were carried out only over $0 \leq r \leq a$ instead of over $0 \leq r \leq \infty$. In the region $0 \leq r \leq a$, we expand

$$L_i X_i^0(r) = \sum_{\beta=0}^1 g_{\beta i} A_{i\beta}(r) + \sum_{a=1}^n h_a^i \eta_a^i(r) \quad (113)$$

involving the coefficients $g_{\beta i}$ and h_a^i . Substituting (111) into (113) and requiring (48) or substituting (111) into (48) yields

$$\mathbf{M}^n \mathbf{A} \boldsymbol{\alpha}^0 + \mathbf{M}^n \mathbf{c}^i = 0 \quad (114)$$

where the column vectors $\boldsymbol{\alpha}$ and \mathbf{c}^i are defined by

$$(\boldsymbol{\alpha}^0)_{\beta} = \alpha_{\beta i}^0 \quad (115)$$

and

$$(\mathbf{c}^i)_a = c_a^i \quad (116)$$

Assume the $A_{i\beta}(r)$ are orthogonal to the $\eta_a^i(r)$. Then we obtain from (6a), (6b), (43), (44), (68), (69), (111), and (113) for very large a

$$\mathbf{M}^n \mathbf{A} \boldsymbol{\alpha}^0 + \mathbf{M}^n \mathbf{c}^i = \left(\frac{a}{2a_0} \right) \mathbf{g} \quad (117)$$

where

$$(\mathbf{g})_{\beta} = g_{\beta i} \quad (118)$$

and $g_{\beta i}$ is proportional to a^{-1} . We show in Appendix 1 that this orthogonality assumption is not necessary. Comparison of (114) and (117) shows we can require \mathbf{g} to equal the null vector only if

$$\begin{vmatrix} M^{AA} & M^{A\eta} \\ M^{\eta A} & M^{\eta\eta} \end{vmatrix} = 0 \quad (119)$$

where the determinant is of order $n + 2$. In general the determinant does not vanish, and we cannot take \mathbf{g} to be the null vector. Instead we minimize its norm $|\mathbf{g}|$ as follows. If $M^{\eta\eta}$ is nonsingular, we eliminate \mathbf{c}^i from (114) and (117) to obtain

$$(M^{AA} - M^{A\eta}M^{\eta\eta-1}M^{\eta A})\alpha^0 = \left(\frac{a}{2a_0}\right)\mathbf{g} \quad (120)$$

Comparing (120) to (103) we see that the 2×2 matrix in (120) is the matrix whose components are given in (67); thus, calling this matrix \mathbf{M} , we can write (120) as

$$\mathbf{M}\alpha^0 = \left(\frac{a}{2a_0}\right)\mathbf{g} \quad (121)$$

We see that \mathbf{g} can be taken as equal to the null vector only if $\text{DET } M = 0$. Multiplying each side of (121) by its adjoint yields

$$\alpha^{0\dagger} \mathbf{Q} \alpha^0 = \left(\frac{a}{2a_0}\right)^2 |\mathbf{g}|^2 \quad (122)$$

where

$$\mathbf{Q} = \mathbf{M}^\dagger \mathbf{M} \quad (123)$$

Now α^0 is chosen to minimize $|\mathbf{g}|$. This means the α^0 used in (112) must be the eigenvector of the Hermitian matrix \mathbf{Q} corresponding to its lowest eigenvalue. Let the other eigenvector of \mathbf{Q} be β .

If α^0 and β are normalized they can be used to construct the 2×2 orthogonal transformation matrix

$$\mu = (\alpha^0 \beta) \quad (124)$$

Although $\mu^\dagger \mathbf{Q} \mu$ is diagonal, it is interesting to point out^{48,49} that the matrix \mathbf{M}' defined as

$$\mathbf{M}' = \mu^\dagger \mathbf{M} \mu \quad (125)$$

is not diagonal. The explicit result obtained from α^0 and (112) is¹⁶

$$t_{MN}^0 = \frac{(M^{11})^2 + (M^{01})^2 - (M^{10})^2 - (M^{00})^2 - \{[M^{00}]^2 + (M^{01})^2 + (M^{10})^2 + (M^{11})^2\}^{1/2} - 4(\text{DET } M)^{1/2}}{2(M^{00}M^{01} + M^{11}M^{10})} \quad (126)$$

Note that we have corrected the typographical error in Ref. 16.

If $M^{\mu\nu}$ is singular, that is, if $E = E_{\mu}^{\nu}$, then the n linear equations (114) fully determine α and the two linear equations (117) are not needed for this purpose. If we define the column vector obtained from (89) by

$$(c^{\mu})_{\alpha} = c_{\alpha}^{\mu} \quad (127)$$

then multiplying (114) by the transpose conjugate of c_{μ}^{ν} yields the single linear equation

$$[c^{\mu}]^{\dagger} M^{\nu A} \alpha^0 = 0 \quad (128)$$

which [with (112)] is identical to (109) of the original Harris method.

The zero-order result obtained from (126) or (128) may be corrected variationally by either the Kohn or the Rubinow variational expression to yield

$$t_{MN}^K = t_{MN}^0 - \frac{2ma_0}{\hbar^2 k} [M^{00} + (M^{01} + M^{10})t_{MN}^0 + M^{11}(t_{MN}^0)^2] \quad (129)$$

or

$$(t_{MN}^R)^{-1} = (t_{MN}^0)^{-1} + \frac{2ma_0}{\hbar^2 k} [(t_{MN}^0)^{-2} M^{00} + (t_{MN}^0)^{-1} (M^{01} + M^{10}) + M^{11}] \quad (130)$$

Harris has pointed out that these expressions are not stationary (see discussion in Section II.C above) and has suggested the use of a different variational expression.⁵⁰ This expression will be called the minimum-norm variational expression and it is

$$(t^{MN} + A)^{-1} = (t^0 + A)^{-1} + \left(\frac{2ma_0}{\hbar^2 k} \right) (t^0 + A)^{-2} I(X_i^0) \quad (131)$$

where

$$A = \frac{M^{00} + t^0 M^{01}}{M^{10} + t^0 M^{11}} \quad (132)$$

It can be verified that $t_K^{MN} = t_K^K$ and that $t_R^{MN} = t_R^R$. Applying (131) and (132) to t_{MN}^0 yields the variationally corrected minimum-norm result t_{MN}^{MN} . Notice that if $\text{DET } M = 0$

$$t_{MN}^0 = t_{MN}^K = t_{MN}^R = t_{MN}^{MN} \quad (133)$$

Nesbet and Oberoi^{48,49} have also considered the problem of the non-stationary nature of the Kohn variational expression when the minimum-norm method is used for t^0 . They have developed a method they call the optimized minimum-norm method. As the final result of the optimized minimum-norm method one calculates the quantity

$$t_{MN}^{OMN} = \frac{\sin \eta_{MN}^0 + t' \cos \eta_{MN}^0}{\cos \eta_{MN}^0 - t' \sin \eta_{MN}^0} \quad (134)$$

where

$$t' = -\frac{2ma_0}{\hbar^2 k} \left[M_{11}' - \frac{(M_{21}')^2}{M_{22}'} \right] \quad (135)$$

G. Methods Involving No Free-Free Integrals

Of all the zero-order and variationally corrected calculational methods discussed above, the original Harris method is the only one that can be carried out without evaluating any free-free integrals. In most cases, the free-free integrals are the most difficult integrals to evaluate. In this section we discuss two other methods in which no free-free integrals need to be evaluated. Unlike the Harris method, these two methods can be applied at any energy for any basis set.

Euler integral methods have been used by Hulthén,⁷ Huang,⁸ Malik,⁵¹ and Moiseiwitsch.⁴⁷ The method to be considered here is a more systematic version of the method used by Huang.⁸ It differs from Huang's and Malik's approaches using Euler integrals in that the wave function is expressed as

$$X_i^0(r) = S_i(r) + t_i^0 C_i(r) + v_i(r) \quad (136)$$

where $v_i(r)$ is a square-integrable function with the boundary condition

$$v_i(0) = 0 \quad (137)$$

The function $v_i(r)$ is eventually determined by expanding it as

$$v_i(r) = \sum_{\alpha=1}^n c_{\alpha}^i \eta_{\alpha}^i(r) \quad (138)$$

where the $\eta_{\alpha}^i(r)$ are square-integrable functions satisfying (45) and the c_{α}^i are coefficients. Substituting (136) into (3) yields

$$-\frac{\hbar^2}{2m} \frac{d^2 v_i}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} + V(r) - E \right] v_i(r) + L_i S_i(r) + t_i^0 L_i C_i(r) = 0 \quad (139)$$

This is a nonhomogeneous differential equation for $v_i(r)$ with homogeneous boundary conditions. It replaces the homogeneous differential equation (3) which had to be solved with nonhomogeneous boundary conditions at large r .

Now we seek a functional $F(r, v_i, v_i')$ where $v_i' = dv_i/dr$. It will be required that the Euler equation

$$\frac{d}{dr} \left(\frac{\partial F}{\partial v_i'} \right) - \frac{\partial F}{\partial v_i} = 0 \quad (140)$$

of this functional be equivalent to (139). It can be seen that the functional we seek is

$$F(r, v_i, v_i') = -\frac{\hbar^2}{4m} [v_i']^2 - \frac{1}{2} \left[\frac{l(l+1)\hbar^2}{2mr^2} + V(r) - E \right] v_i^2 - v_i [L_i S_i(r) + t_i^0 L_i C_i(r)] \quad (141)$$

Therefore, by Euler's theorem, the solution of (139) may be obtained by minimizing the Euler integral

$$\Gamma_i = \int_0^\infty dr F(r, v_i, v_i') \quad (142)$$

Substituting (138) and (141) into (142) yields

$$\Gamma_i(c_1^i, c_2^i, \dots, c_n^i, t_i^0) = \frac{1}{2} \sum_{ab} c_a^i c_b^i A_{ab}^i - \sum_a c_a^i (M_{a0}^{\eta^A} + t_i^0 M_{a1}^{\eta^A}) \quad (143)$$

where

$$A_{ab}^i = \int_0^\infty dr \left\{ -\frac{\hbar^2}{2m} \frac{d\eta_a^i}{dr} \frac{d\eta_b^i}{dr} - \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r) - E \right] \eta_a^i(r) \eta_b^i(r) \right\} \quad (144)$$

To minimize (143) we require

$$\frac{\partial \Gamma_i}{\partial c_b^i} = 0 \quad b = 1, 2, \dots, n \quad (145)$$

$$\frac{\partial \Gamma_i}{\partial t_i^0} = 0 \quad (146)$$

This yields the $(n+1)$ nonhomogeneous linear equations

$$\sum_{a=1}^n c_a^i A_{ab}^i - t_i^0 M_{b1}^{\eta^A} = M_{b0}^{\eta^A} \quad (147)$$

and

$$\sum_{a=1}^n c_a^i M_{a1}^{\eta^A} = 0 \quad (148)$$

for the $n+1$ unknowns. The t_i^0 determined this way is called t_{EI}^0 . Extending a suggestion of Hulthén and Olsson⁵² we may variationally correct t_{EI}^0 through first order using the Kohn variational expression, yielding t_{EI}^K . Such a correction involves the calculation of free-free integrals.

Ladányi, Lengyel, and Szondy⁵³ have proposed using the method of moments for scattering problems. In this case we use the $n+1$ equations

$$\int_0^\infty dr w_a(r) L_i X_i^0(r) = 0 \quad (149)$$

where the $w_a(r)$ are "weight functions" to determine the $n + 1$ parameters in $X_l^0(r)$. For certain choices of trial function and weight functions, this method may be made to yield the zero-order Kohn or zero-order Rubinow method. Ladányi et al., however, recommend that all the weight functions be square-integrable. This eliminates all free-free integrals.

As an example of the method of moments we consider the trial function (40) and the solution of equations (48) and

$$\int_0^\infty dr \eta_{n+1}^*(r) L_l X_l^0(r) = 0 \quad (150)$$

for the unknown coefficients c_a^l and t_l^0 . Equation (150) was obtained by using the basis functions [see (40)], including one more basis function than is used in $X_l^0(r)$, as weight functions in (149). The t_l^0 obtained by this method is called t_{MM}^0 . We suggest that improved results can be obtained using the Kohn, Rubinow, Percival, or minimum-norm variational expression to correct t_{MM}^0 . In this case, however, free-free integrals must be calculated.

H. Discussion of Above Methods and the Anomaly-Free Method

In this section results are presented for a model problem, namely, the scattering of a particle with the mass of the electron and orbital angular momentum l equal to zero off the potential

$$V = -2\mathcal{R}e^{-r/a_0} \quad (151)$$

where \mathcal{R} is the Rydberg energy and a_0 is the bohr. The exact solution⁵⁴ to this problem exhibits no resonances. The trial function is

$$X_0^0(r) = a_0^{-1/2} \left[\sin kr + t_0^0(1 - e^{-r}) \cos kr + \sum_{a=1}^n c_a^0 \left(\frac{r}{a_0}\right)^a e^{-2.5r/a_0} \right] \quad (152)$$

where $n = 6$ for all results except some of those in Table IV. The phase shift is always given mod π in discussing the results. For $n = 6$, the lowest two eigenvalues E_μ^0 of M^{nn} correspond using

$$E_\mu^l = \frac{\hbar^2 k_\mu^2}{2m} \quad (153)$$

to $k_1 = 0.264362a_0^{-1}$ and $k_2 = 1.042019a_0^{-1}$.

We have done calculations for k in the range 0.1 to $1.0a_0^{-1}$ designed to illustrate the various facets of the methods. Similar calculations were presented by Nesbet.¹³ First we discuss the spurious singularities which are of great historical importance. Our explanations follow closely the work of

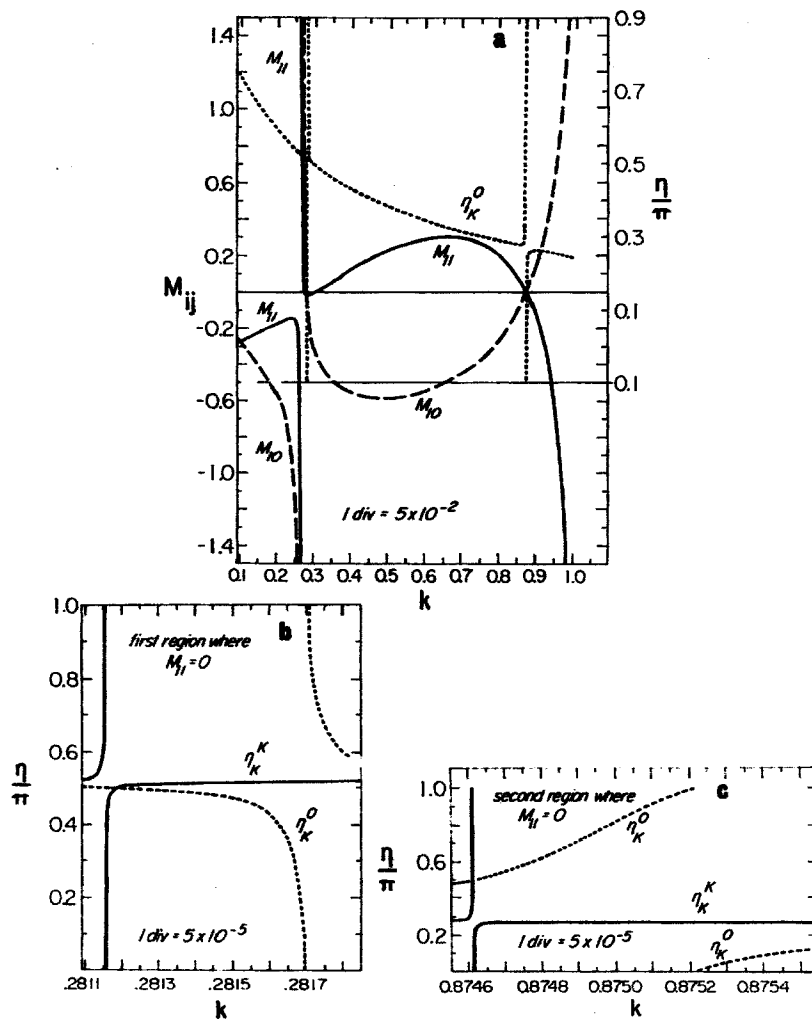


Fig. 1. (a) The quantities M^{11} and M^{10} (in Ry) and the zero-order Kohn phase shift η_K^0 (in radians) are shown as functions of momentum k (in atomic units) for scattering of a particle with the mass of an electron from an attractive exponential potential. The scale on the left applies to the $M^{\alpha\beta}$ and the scale on the right to η_K^0 . On the scale of (a), η_K^0 and η_K^K could not be distinguished except near the regions where M^{11} is not about equal to zero. (b) and (c) With a more expanded abscissa these are the only two regions where variationally corrected Kohn phase shift η_K^K differs appreciably from η_K^0 . The $M^{\alpha\beta}$ are labeled $M_{\alpha\beta}$ as in Ref. 13.

Nesbet's *Analysis of the Harris Variational Method in Scattering Theory*.¹³ In this work, however, Nesbet missed a pseudoresonance in his Rubinow method calculations because it was too narrow to be seen in his Table V. This makes Sections VI and VII of his paper a little confusing. The mistake was corrected by Harris and Michels.¹⁰ The correct conclusions of Nesbet's work are as follows: t_K^K and t_R^R show irregular behavior (i.e., the computed values show a wild fluctuation) when E is near E_μ^1 . In addition, t_K^K and t_R^R have poles at the zeroes, respectively, of M^{11} and M^{00} . For numerical accuracy, t_K^K or t_H should be used when

$$R = \frac{|M^{00}|}{|M^{11}|} \quad (154)$$

is less than unity and t_R^R or t_H should be used when R is greater than unity. The following is an elaboration and continuation of this analysis.

Fig. 1a shows the zero-order Kohn phase shift and M^{11} and M^{10} for $k = 0.1-1.0a_0^{-1}$ and $n = 6$. The zero-order Kohn phase shift shows in one energy region a rapid increase by π (a resonance) and in another energy region a rapid decrease by π (an antiresonance). Since the exact solution⁵⁴ has no resonances the resonance is spurious and may be called a pseudoresonance. Further, an antiresonance as sharp as the one shown is forbidden by causality⁵⁵ and thus the antiresonance is spurious. It may be called a pseudoantiresonance. These spurious results may both be called spurious singularities since a change by π of the phase shift in an energy interval causes both the tangent and the cotangent of the phase shift to become zero (singular) within that interval. The plot shows that the spurious singularities both occur near energies at which the matrix elements M^{11} and M^{10} become zero. Since η_K^0 converges to the exact result as n is increased, (78) shows that the zeroes of M^{11} and M^{10} coincide in this limit except in regions where the phase shift goes smoothly through $\pi/2$ or 0. For finite n these zeroes are shifted slightly relative to one another. It is this shift that causes the spurious zeroes. Fig. 1b is a blowup plot of the pseudoantiresonance shown in Fig. 1a, and Fig. 1c is a blowup of the pseudoresonance shown in Fig. 1a. From Fig. 1b we see that even though the zero-order Kohn phase shift exhibits pseudoantiresonance structure the variationally corrected Kohn phase shift shows pseudoresonance structure. Also note from Figs. 1b and 1c that the spurious zeroes of η_K^K and η_K^0 are not centered about the same k .

The nature of the spurious results (increases and decreases of η by π as opposed to $\pi/2$, 2π , or some other values) and their general location are explained as follows. Nesbet¹³ has proved that when E equals E_μ^1 (i.e., when $M^{\alpha\beta}$ has a zero eigenvalue), $\text{DET } M$ and all four $M^{\alpha\beta}$ ($\alpha, \beta = 0, 1$) have

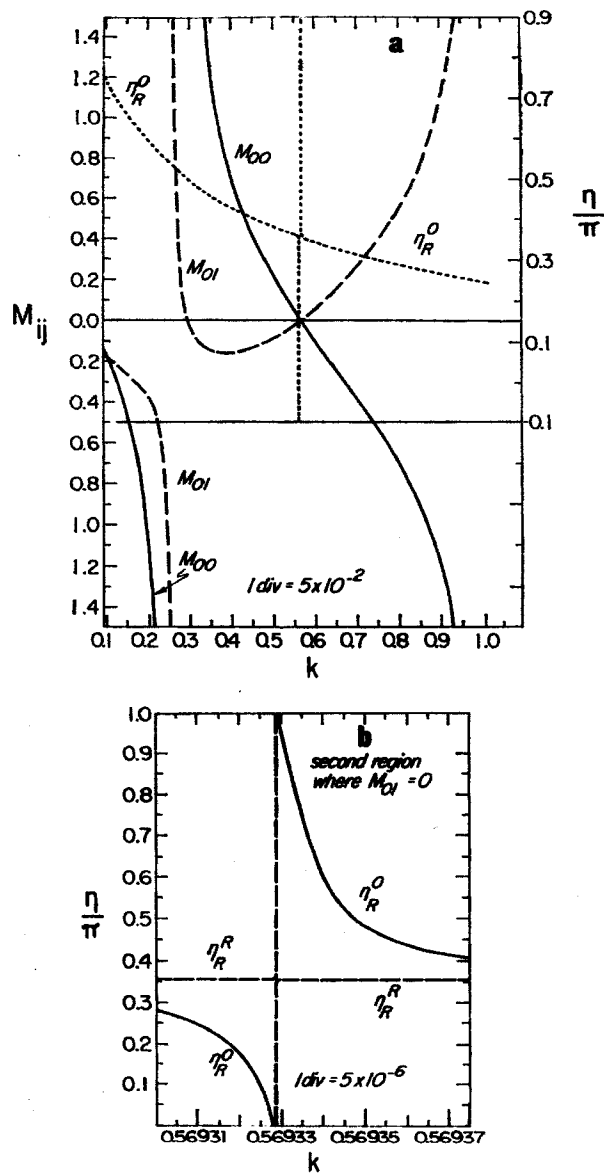


Fig. 2. (a) The integrals M^{00} and M^{01} (in Ry) and the zero-order Rubinov phase shift η_R^0 (in radians) are shown as functions of momentum k (in atomic units) for scattering of a particle with the mass of an electron from an attractive exponential potential. The scale on the left applies to $M^{\alpha\beta}$ and the scale on the right to η_R^0 . On the scale of part a, η_R^0 and η_R^R could not be distinguished except near the region where M^{00} is equal to zero. (b) With a more expanded abscissa this is the only region where the variationally corrected Rubinov phase shift η_R^R differs appreciably from η_R^0 . The $M^{\alpha\beta}$ are labeled $M_{\alpha\beta}$ as in Ref. 13.

poles of odd order. This behavior is illustrated graphically in Figs. 1a, 2a, and 3. Because of these odd-ordered poles, $\text{DET } M$ and each M^{ab} tend to pass through every value in the range $-\infty$ to $+\infty$ in the vicinity of each zero eigenvalue of M^{ab} . Thus, for example, M^{10} and M^{11} each tend to pass through zero near each zero eigenvalue of M^{ab} . By (78), this means η_K^0 tends to pass through both 0 and $\pi/2$ near each zero eigenvalue of M^{ab} . Depending on the order in which M^{10} and M^{11} reach zero, this will be manifest as a resonancelike or antiresonancelike behavior. As explained above, in the limit where the basis set is large enough to represent the exact solution, if the structure is spurious the zeroes of M^{10} and M^{11} coincide and the structure disappears. Thus as the basis set is made more accurate, the zeroes of M^{10} and M^{11} move closer (except near real resonances) and thus the energies at which η_K^0 equals 0 and $\pi/2$ move closer; that is, the width of the pseudoresonance or pseudoantiresonance becomes zero.

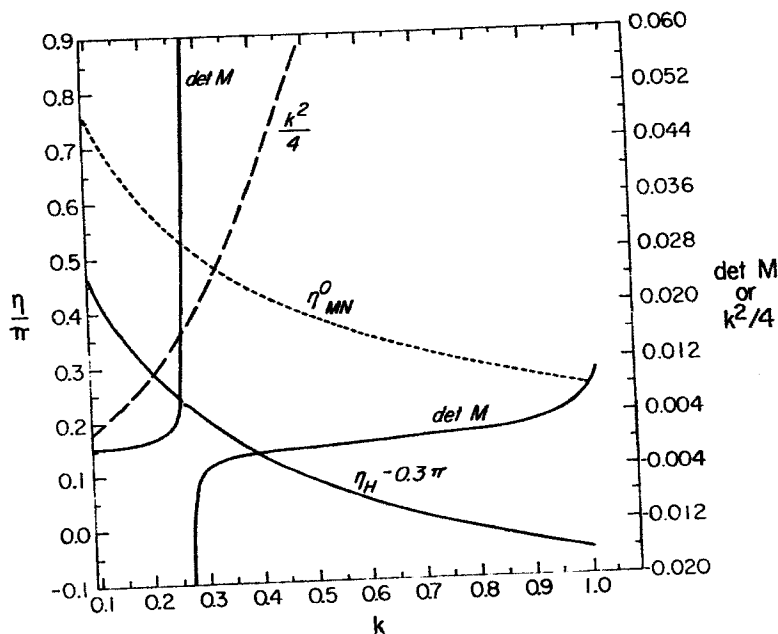


Fig. 3. The left- and right-hand sides of inequality (77) in Ry^2 , the zero-order minimum-norm phase shift η_{MN}^0 (in radians), and the Hulthén phase shift η_H (in radians) as functions of momentum k (in atomic units) for scattering of a particle with the mass of an electron from an attractive exponential potential. The curve labeled $\text{det } M$ (following Ref. 13) is $\text{Ry}^{-2} \text{DET } M$ and has been extended beyond $k = 1.0 a_0^{-1}$ to indicate more clearly where its pole is.

Comparison of (78) and (80a) shows η_K^0 and η_K^K are $\pi/2$ at the same place, namely, where M^{11} vanishes (see Figs. 1b and 1c for examples). Since both M^{10} and $(-2ma_0 \text{ DET } M/\hbar^2 k)$ tend to take on every value from $-\infty$ to $+\infty$ near a zero eigenvalue of M^n , they tend to cross; thus t_K^K given by (80a) tends to have a zero near every zero eigenvalue of M^n . (Alternatively,⁵⁶ (80b) shows that t_K^K , like t_K^0 , cannot vary smoothly near a zero of M^{11} unless M^{10} also vanishes.) Thus η_K^K , like η_K^0 , tends to pass through both 0 and $\pi/2$ near each zero eigenvalue of M^n . This is the reason η_K^K shows resonance, pseudo-resonance, or pseudoantiresonance behavior near each zero eigenvalue of M^n . Figs. 1b and 1c illustrate the important fact that the width of the spurious structure in η_K^K tends to be narrower than the width of the spurious structure in η_K^0 .

Similar spurious singularities should occur in η_R^0 and η_R^K for the same kinds of reasons. Fig. 2a is a graph similar to Fig. 1a except that quantities pertinent to the Rubinow method have been plotted. Fig. 2a shows that the zero-order phase shift varies smoothly through the eigenvalue but exhibits a pseudoantiresonance around k equal to $0.55a_0^{-1}$. Note again that the pseudoantiresonance occurs in the region where both M^{00} and M^{01} vanish. The first zero of M^{01} just causes the phase shift to go smoothly through $\pi/2$. Thus a zero of M^{01} that is not close to a zero of M^{00} does not cause spurious structure. Thus the spurious structure tends to occur near zero eigenvalues of M^n . This tendency is destroyed if the "background" M^{01} or M^{10} is near zero; however, using (70) we see the background M^{01} and M^{10} will not both be near zero for the same energy. Thus the tendency of the spurious structure to occur near a zero eigenvalue of M^n will not be destroyed in both the Kohn and Rubinow methods near one zero eigenvalue of M^n .

Fig. 2b shows that the zeroes of η_R^0 and η_R^K occur at the same value of k , namely, where M^{00} is zero. This is explained by (79) and (83). Further the rapid changes by π of η_R^0 and η_R^K are centered about the same k in this case.

The fact that the zeroes of M^{00} and M^{01} (which when they occur near each other cause structure in the Rubinow method) and the zeroes of M^{10} and M^{11} (which when they occur near each other cause structure in the Kohn method) do not generally occur in the same energy regions (the exception being when there really is a resonance and the basis set is accurate enough that both the Kohn and Rubinow methods show the resonance) forms the basis of Nesbet's original method, also called the anomaly-free method.^{13,14} Nesbet suggested calculating the ratio R [see (154)] and using the Kohn method when R is less than unity and the Rubinow method otherwise. One possible difficulty with using this

procedure can be seen as follows. Fig. 1 shows M^{11} may be very large at energies very near to the spurious singularities identified by its zeroes. If this occurs where the accurate phase shift is passing smoothly through $0(\text{mod } \pi)$, then M^{00} will be small but the Rubinow method may have no spurious structure at this or nearby energies.⁵⁷ In this case R will be less than unity but the Rubinow method would be preferred. An alternative method to avoid spurious singularities is to calculate η_K^K , η_R^R , η_H , and one of the minimum-norm phase shifts. If three out of four of these quantities agree fairly well, they are probably free of spurious singularities. If no three out of four agree, the basis set should be improved.

Fig. 3 shows a plot of $(\mathcal{R}^{-2} \text{DET } M)$ against $(\hbar^2 k/4m \mathcal{R})^2$. Since $\text{DET } M$ tends to zero as the basis set becomes more accurate, it is generally small for a basis set that is fairly accurate. However, due to the odd-ordered pole of $\text{DET } M$ near each zero eigenvalue of M^{nn} , there will be a region near each zero eigenvalue of M^{nn} in which (77) is true. This region will be bounded on one side by the zero eigenvalue of M^{nn} and on the other by the energy where (77) with an equal sign holds. In this region then t_H will be complex. Fig. 3 shows a plot of η_H which has a narrow break in the energy region just below the first zero eigenvalue of M^{nn} . In this region, (77) is true. We have observed that the result η_H often shows a change in slope very close to the break.

Fig. 3 also shows that η_{MN}^0 varies smoothly as one passes through the zero eigenvalue of M^{nn} . The denominator of (126) vanishes once in the energy region shown in Fig. 3; namely, it vanishes where η_{MN}^0 passes smoothly through $\pi/2$.

Fig. 4 is a plot of the variational corrections

$$\Delta_I^J = \eta_I^J - \eta_I^0 \quad (155)$$

These corrections are generally small but become large in the regions of spurious structure in the results. The spurious structure in η_K^K and η_R^R seen in Figs. 1 and 2 is seen again here in Δ_K^K and Δ_R^R . In the energy region shown, Δ_{MN}^R is always small, indicating there is no spurious structure in η_{MN}^R . However, the figure shows there is one pseudo-resonance in η_{MN}^K . Thus the use of the Kohn variational expression to correct the singularity-free η_{MN}^0 has resulted in introducing a pseudo-resonance. In other cases (no examples are shown), the Rubinow variational expression introduces spurious singularities into the minimum-norm method. The figure shows, however, that η_{MN}^{MN} is free of spurious singularities. Nesbet and Oberoi⁴⁸ have pointed out that t_{MN}^{0MN} is not free of the spurious singularities.

Fig. 4 shows that Δ_R^K and Δ_K^R have two regions each of spurious

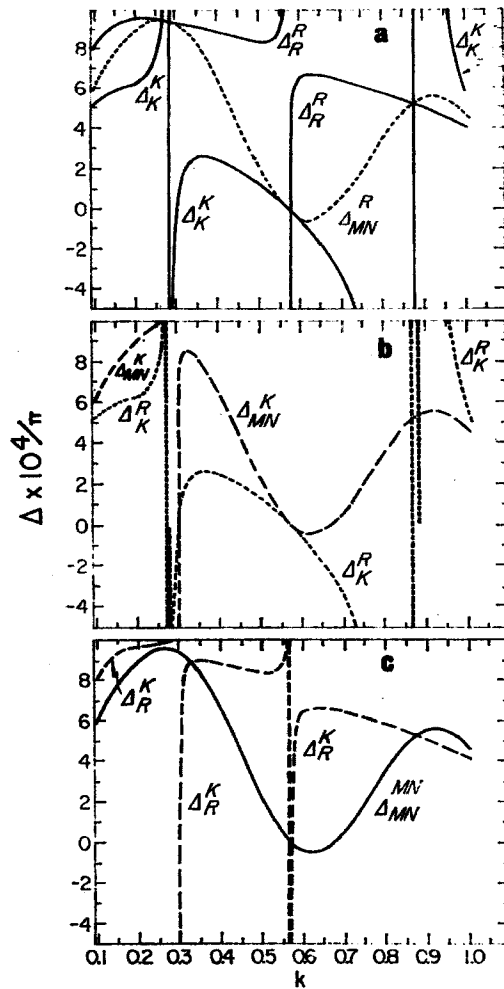


Fig. 4. The first-order corrections Δ_A^B (in radians) to the zero-order phase shift (mod π) in method A as corrected using variational expression B as functions of k (in atomic units) for scattering of a particle with the mass of an electron from an attractive exponential potential. The abbreviations for the methods are K = Kohn, R = Rubinow, and MN = minimum-norm.

structure. It can be shown that

$$\Delta_R^K = -\left(\frac{2m}{\hbar^2 k}\right) t_R^0 \frac{\text{DET } M}{M^{01}} \quad (156)$$

and thus Δ_R^K has a pole if and only if $M^{01} = 0$. This happens twice in the energy region shown, once because of a pseudoantiresonance in t_R^0 and once because η_R^0 passes smoothly through $\pi/2$. Further analysis shows that the Kohn variational correction does not make the region of spurious structure in η_R^0 narrower. In comparison, Fig. 2b shows that although the Rubinow variational correction does not remove the spurious structure it does make it narrower. Further the Kohn variational correction introduces a new region of spurious structure not found in η_R^0 . The Rubinow variational correction does not introduce new regions of spurious structure not found in η_R^0 . We conclude η_R^R is to be preferred to η_R^K . A similar analysis would show η_K^K is to be preferred to η_K^R .

Figs. 5a and 5b show with expanded abscissas two regions where the nonstationary methods lead to unusual spurious structure. These figures show spurious structures in η_R^K and η_K^R which are wider than those in η_K^K , η_R^R , η_K^0 , and η_R^0 . To analyze these structures we write (81) and (82) as

$$t_R^K = \frac{-M^{00}[M^{01} + (2ma_0/\hbar^2 k) \text{DET } M]}{(M^{01})^2} \quad (81a)$$

and

$$t_K^R = \frac{(M^{10})^2}{M^{11}[-M^{10} + (2ma_0/\hbar^2 k) \text{DET } M]} \quad (82a)$$

respectively. Equation (81a) and Figs. 1 through 3 can be used to show that η_R^K must pass successively through $0(\text{mod } \pi)$ when M^{00} is zero, through $(\pi/2)(\text{mod } \pi)$ when M^{01} is zero, and through $0(\text{mod } \pi)$ when $[M^{01} + (2ma_0/\hbar^2 k) \text{DET } M]$ is zero and that these three locations are all very near to $k = 0.57a_0^{-1}$. Notice that at the zeroes of M^{01} and M^{00} , η_R^K equals η_R^0 but η_R^K has additional spurious behavior due to an extra zero of the denominator. This is not accidental; we can expect the zeroes of the three factors in t_R^K will often occur near each other near a zero eigenvalue of M^m . A similar analysis holds for Fig. 5a and t_K^R .

Note that Figs. 4c and 4b show that η_R^K and η_{MN}^K exhibit spurious structure near $k = 0.30a_0^{-1}$. These are attributed to unphysical zeroes of the numerators in the formulas for t_R^K and t_{MN}^K . The former has a zero numerator near $k = 0.299245a_0^{-1}$, and the latter has a zero numerator near $k = 0.299270a_0^{-1}$. In this region ($0.299245a_0^{-1} \leq k \leq 0.299270a_0^{-1}$) the background phase shift has a value of 0.5018π , and passes smoothly through $\pi/2$ near $k = 0.30160a_0^{-1}$. The zero numerators mentioned above

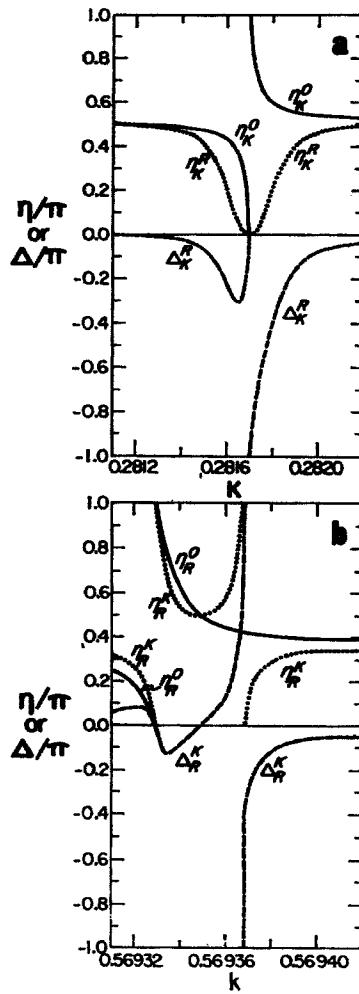


Fig. 5. (a) Phase shifts η_K^0 and η_K^R (in radians) and first-order correction Δ_K^R (in radians) as functions of wave number k (in atomic units) for the potential scattering problem of Section II. The range of the abscissa is chosen to more clearly illustrate spurious structure shown in Fig. 4b. (b) Phase shifts η_k^0 and η_k^R (in radians) and first-order correction Δ_k^R (in radians) as functions of wave number k (in atomic units) for the potential scattering problem of Section II. The range of the abscissa is chosen to more clearly illustrate spurious structure shown in Fig. 4c.

cause η_R^K and η_{MN}^K to increase to a value of $\pi(\text{mod } \pi)$ near $k = 0.299245a_0^{-1}$ and $k = 0.299270a_0^{-1}$, respectively. Then η_{MN}^K and η_R^K increase to the background phase shift ($\text{mod } \pi$) for k a little larger than $0.30160a_0^{-1}$. A plot of Δ_R^K or Δ_{MN}^K with a more expanded ordinate would show a discontinuity where Δ changes from 0.4982π to -0.5018π . It is interesting to note that these variationally corrected phase shifts have spurious structures but their zero-order counterparts remain smooth throughout the region. Also note that η_R^K and η_{MN}^K do not attain the value of $\pi/2$ in this region.

The quantity t_{OAF} appearing in Tables I-IV is discussed in Section II.I.

Table I illustrates the behavior of several of the computed tangents of the phase shifts near E_1^0 . We see that in all cases the results vary smoothly. This smooth behavior is a result of the fact, which has been discussed, that the pseudoresonances and pseudoantiresonances do not occur at zero eigenvalues of $M^{\eta\eta}$ but rather "nearby" where $M^{\alpha\beta}$ elements have correlated

TABLE I

The Values of $\det M^{\eta\eta}$, $\text{DET } M$, M^{00} , M^{01} , M^{11} , and the Tangents of the Phase Shifts as Calculated by Various Methods Discussed in the Text for the Potential Scattering Problem of Section II. Values of k Were Picked so That the Incident Energies Bracket an Eigenvalue of the Bound-Bound Matrix $H^{\eta\eta}$. Energies are in Hartrees and k is in a_0^{-1}

k	0.26436165	0.26436170	0.26436175	0.26436180
$\det M^{\eta\eta}$	8.0189211(-23) ^a	3.2692534(-23)	-1.4803981(-23)	-6.2300675(-23)
$\text{DET } M$	2.3254257(+2)	5.7038538(+2)	-1.2596558(+3)	-2.9932065(+2)
M^{00}	-5.7978167(+5)	-1.4221058(+6)	3.1405237(+6)	7.4625612(+5)
M^{01}	-5.5541916(+4)	-1.3623467(+5)	3.0085495(+5)	7.1489513(+4)
M^{11}	-5.3208168(+3)	-1.3051001(+4)	2.8821199(+4)	6.8485076(+3)
t_R^0	-10.438632	-10.438648	-10.438664	-10.438680
t_R^K	-10.107992	-10.108008	-10.108012	-10.108028
t_R^R	-10.118143	-10.118159	-10.118164	-10.118180
t_R^P	-10.118053	-10.118069	-10.118074	-10.118089
t_P^0	-10.438633	-10.438648	-10.438664	-10.438680
t_R^R	-10.118143	-10.118159	-10.118164	-10.118180
t_R^K	-10.107992	-10.108008	-10.108012	-10.108028
t_H	^b	^b	-10.437435	-10.436164
t_P^0	-10.438633	-10.438648	-10.438664	-10.438680
t_P^P	-10.118053	-10.118069	-10.118074	-10.118089
t_{MN}^0	-10.438633	-10.438648	-10.438664	-10.438680
t_{MN}^K	-10.107992	-10.108008	-10.108012	-10.108028
t_{MN}^R	-10.118143	-10.118159	-10.118164	-10.118180
t_{MN}^{MN}	-10.118054	-10.118069	-10.118075	-10.118090
t_{MN}^{MN}	-10.118054	-10.118069	-10.118075	-10.118090
t_{E1}^0	-10.438624	-10.438645	-10.438666	-10.438686
t_{E1}^K	-10.107985	-10.108001	-10.108017	-10.108033
t_{MM}^0	-10.438633	-10.438648	-10.438664	-10.438680
t_{MM}^K	-10.107988	-10.108002	-10.108017	-10.108031
t_{AF}^{AF}	-10.118143	-10.118159	-10.118164	-10.118180
t_{OAF}	-10.118054	-10.118070	-10.118074	-10.118090
t_{exact}	-10.116471	-10.116486	-10.116500	-10.116515

^a Numbers in parentheses are multiplicative powers of 10.

^b Complex (nonphysical) tangent.

TABLE II

The values of $\det M^{nn}$, $\text{DET } M$, M^{00} , M^{01} , M^{11} , and Tangents of the Phase Shift as Calculated by Various Methods Discussed in the Text for the Potential Scattering Problem of Section II. Values of k were Picked Such That $\text{DET } M$ Passes Through Zero as a Function of Momentum. Energies are in Hartrees and k is in a_0^{-1}

k	0.5675	0.5700	0.5725	0.5750
$\det M^{nn}$	-3.0274153(-16) ^a	-3.0459831(-16)	-3.0643175(-16)	-3.0824155(-16)
$\text{DET } M$	-6.4422255(-6)	-3.2612590(-6)	-6.5297276(-8)	3.1459858(-6)
M^{00}	2.7988344(-3)	-1.0242731(-3)	-4.8290998(-3)	-8.6162553(-3)
M^{01}	-1.3655824(-3)	4.8366802(-4)	2.3512792(-3)	4.2372438(-3)
M^{11}	1.3680930(-1)	1.3753433(-1)	1.3824325(-1)	1.3893592(-1)
t_K^0	2.0495537	2.1177192	2.0538181	2.0334575
t_K^K	2.0842025	2.0687764	2.0536189	2.0387227
t_K^R	2.0842025	2.0687764	2.0536189	2.0397227
t_K^P	2.0842025	2.0687764	2.0536189	2.0387227
t_R^0	2.0495537	2.1177192	2.0538181	2.0334575
t_R^R	2.0842053	2.0687745	2.0536189	2.0387225
t_R^K	2.0836292	2.0676165	2.0536189	2.0387089
t_H	2.0842024	2.0687764	2.0536189	2.0387227
t_P^0	2.0833340	2.0683340	2.0536100	2.0391558
t_P^P	2.0842025	2.0687764	2.0536189	2.0387227
t_{MN}^0	2.0840331	2.0686938	2.0536173	2.0387965
t_{MN}^K	2.0842025	2.0687764	2.0536189	2.0387227
t_{MN}^R	2.0842025	2.0687764	2.0536189	2.0387227
t_{MN}^{MN}	2.0842025	2.0687764	2.0536189	2.0387227
t_{MN}^{OMN}	2.0842025	2.0687764	2.0536189	2.0387227
t_{MI}^0	2.0621128	2.0444639	2.0271283	2.0100965
t_{MI}^K	2.0839707	2.0684931	2.0532800	2.0383245
t_{MN}^0	2.0777692	2.0626769	2.0478431	2.0332608
t_{MN}^K	2.0841835	2.0687589	2.0536028	2.0387078
t_{AF}^{AF}	2.0842025	2.0687764	2.0536189	2.0334575
t_{OAF}	2.0842025	2.0687764	2.0536189	2.0387227
t_{exact}	2.0842069	2.0687798	2.0536219	2.0387254

^a Numbers in parentheses are multiplicative powers of 10.

zeroes. It is especially interesting that t_{MN}^0 , which at the eigenvalue is t_{Harris} , varies smoothly in this energy region. It is also interesting to note the much greater accuracy of the variationally corrected results when compared to the zero-order results.

Table I also illustrates (110). In addition it shows that t_P^0 may be added to the list in that equation.

Table II illustrates many of the computed tangents of the phase shifts near a zero of $\text{DET } M$. This provides an illustration of (87) and (133). In addition it shows that t_P^P , t_{OAF} , and t_{MN}^{OMN} may be added to the lists in those equations.

Table III further illustrates the possible accuracies attainable by the various methods. Note that much more accurate values are obtained from variationally corrected results than from zero-order results. In particular, if the Kohn, Rubinow, Percival, minimum-norm, or Euler integral methods or the method of moments are used without a variational

TABLE III
 The Values of $\det M^m$, $\text{DET } M$, M^{00} , M^{01} , M^{11} , and the Tangents of the Phase Shifts Calculated by Various Methods Discussed in the Text for the Potential Scattering Problem of Section II for Various Values of k . Energies are in Hartrees and k is in a_0^{-1}

k	0.15	0.25	0.35	0.45	0.55
$\det M^m$	9.1036780(-17) ^a	1.3413482(-17)	-8.7504072(-17)	-1.9487821(-16)	-2.8911621(-16)
$\text{DET } M$	6.6835540(-5)	1.2576473(-3)	-3.1940408(-4)	-1.4703525(-4)	-2.8317410(-5)
M^{00}	-2.3153279(-1)	-3.2721365	6.2225763(-1)	2.2012822(-1)	3.0126828(-2)
M^{01}	-1.3179002(-1)	-4.5252914(-1)	-7.0271727(-2)	-6.6204382(-2)	-1.3794608(-2)
M^{11}	-1.1799494(-1)	-8.0253335(-2)	2.7185306(-2)	8.6912848(-2)	1.3129464(-1)
t_{K^0}	-1.7525330	-7.1961464	9.0222171	3.3505332	2.1995918
t_{K^K}	-1.7449806	-7.0707818	9.0893550	3.3580521	2.2003761
t_{K^R}	-1.7450130	-7.0729283	9.0898584	3.3580690	2.2003763
t_{K^P}	-1.7450051	-7.0728881	9.0898523	3.3580677	2.2003763
t_{F^0}	-1.7568310	-7.2307752	8.8550212	3.3249797	2.1839568
t_{F^R}	-1.7450314	-7.0735084	9.0811453	3.3581271	2.2003820
t_{F^K}	-1.7449516	-7.0700118	9.0850125	3.3577999	2.2002594
t_{F^H}	-1.7448887	-7.0586424	9.0886691	3.3580304	2.2003758
t_{F^0}	-1.7553792	-7.2299461	8.8620146	3.3322018	2.1966600
t_{F^P}	-1.7450143	-7.0734440	9.0910691	3.3581058	2.2003772
t_{MN^0}	-1.7549206	-7.2297241	8.8771385	3.3411921	2.1994221
t_{MN^K}	-1.7449717	-7.0700579	9.0860854	3.3580184	2.2003761
t_{MN^R}	-1.7450278	-7.0735079	9.0811221	3.3581036	2.2003765
$t_{MN^{MN}}$	-1.7450089	-7.0734274	9.0909030	3.3580794	2.2003761
t_{MN^0}	-1.7450143	-7.0734445	9.0810686	3.3581058	2.2003772
t_{E^0}	-1.6579729	-6.7482295	15.5206952	3.5847924	2.1953115
t_{E^K}	-1.7309131	-6.9419690	2.5291187	3.3568541	2.2003673
t_{E^R}	-1.7461007	-7.2140997	8.7608185	3.3158178	2.1913031
t_{MM^K}	-1.7449155	-7.0705748	9.0787405	3.3575866	2.2003433
$t_{AF^{AF}}$	-1.7450314	-7.0735084	9.0911453	3.3581271	2.2003761
t_{OAF}	-1.7450143	-7.0734445	9.0910685	3.3581058	2.2003772
t_{exact}	-1.7449393	-7.0726191	9.0918095	3.3581425	2.2003827

^a Numbers in parentheses are multiplicative powers of 10.

TABLE IV

The Tangents of the Phase Shifts for the Various Methods Discussed in the Text for the Potential Scattering Problem of Section II at $k = 0.55\epsilon_0^{-1}$ as a Function of the Number of Basis Functions used. At this Value of k the Exact Tangent of the Phase Shift is Given by $t_{\text{exact}} = 2.2003827$. Energies are in Hartrees

n	0	2	4	6	8	10	12
det M^M	0.0	1.2842504(-4)	-3.7528351(-11)	-2.8911621(-16)	-5.9559695(-21)	-4.65214224(-24)	6.5801930(-24)
DET M	1.0728098(-3)*	4.9480633(-3)	-5.5208351(-3)	-2.8317410(-5)	2.9448730(-5)	1.9167492(-5)	-7.4574873(-7)
M_{00}^0	-2.7375566(-1)	-3.8358337(-1)	1.4233691	3.0126829(-2)	-1.8205262(-1)	-6.8379396(-1)	3.2180758(-1)
M_{01}^0	1.3169744(-1)	1.9288660(-1)	-6.6702822(-1)	-1.3794608(-2)	8.2843936(-2)	3.1083106(-1)	-1.4625344(-1)
M_{11}^0	6.5020649(-2)	2.8391510(-2)	4.3788051(-1)	1.3129464(-1)	8.7279793(-2)	-1.6315694(-2)	1.9144677(-1)
I_K^0	2.2039546	2.8921814	2.1528112	2.1995918	2.2016101	2.1961097	2.2003685
$I_{K'}^0$	2.1439563	2.2584372	2.1986902	2.2003761	2.2003832	2.2003817	2.2003827
$I_{K''}^0$	2.1455464	2.03723453	2.1996892	2.2003763	2.2003839	2.2003900	2.2003827
$I_{K^*}^0$	2.1452790	2.3614951	2.1995098	2.2003763	2.2003838	2.2003886	2.2003827
$I_{K^*}^0$	2.0786710	1.9886470	2.1338963	2.1839568	2.1975373	2.1998898	2.2003419
$I_{K^*}^0$	2.1421248	2.1932379	2.2001139	2.2003820	2.2003816	2.2003827	2.2003827
$I_{K^*}^0$	2.1402452	2.1741532	2.1981209	2.2002594	2.2003779	2.2003826	2.2003827
$I_{K^*}^0$	2.1430802	2.2104555	2.1957556	2.2003758	2.2003827	2.2003828	2.2003827
$I_{K^*}^0$	2.0386340	1.9133457	2.1383369	2.1966500	2.1937742	2.1998012	2.2003318
$I_{K^*}^0$	2.1415288	2.1874769	2.1997742	2.2003772	2.2003801	2.2003826	2.2003827
$I_{K^*}^0$	2.1041835	2.0145743	2.1396152	2.1994221	2.1996814	2.1998789	2.2003587
$I_{K^*}^0$	2.1416028	2.1789209	2.1984131	2.2003761	2.2003820	2.2003825	2.2003827
$I_{K^*}^0$	2.1422803	2.1935190	2.2000746	2.2003765	2.2003822	2.2003827	2.2003827
$I_{K^*}^0$	2.1425068	2.1952952	2.1996741	2.2003761	2.2003824	2.2003827	2.2003827
$I_{K^*}^0$	2.1415407	2.1875236	2.1997719	2.2003772	2.2003801	2.2003826	2.2003827
$I_{K^*}^0$	b	1.6705050	2.1436854	2.1953115	2.1947616	2.2023810	2.1985242
$I_{K^*}^0$	b	2.1043494	2.1985634	2.2003673	2.2003683	2.2003840	2.2003803
$I_{K^*}^0$	1.0740540	2.1478812	2.1274896	2.1913031	2.2012906	2.2001552	2.2003152
$I_{K^*}^0$	1.8421008	2.2012430	2.1976699	2.2003433	2.2003831	2.2003827	2.2003827
$I_{K^*}^0$	2.1421248	2.1932379	2.20011387	2.2003761	2.2003816	2.2003827	2.2003827
$I_{K^*}^0$	2.1415157	2.1871933	2.1997718	2.2003772	2.2003801	2.2003826	2.2003827

^a Numbers in parentheses are multiplicative powers of 10.

^b Undefined.

correction to t_i^0 , one finds a larger basis set is required than for variationally corrected calculations. That is, zero-order calculations converge slower than first-order ones.

Note that neither the Euler integral method nor the method of moments eliminates pseudoresonances and pseudoantiresonances. Table III gives values of t_{EI}^0 and t_{MM}^0 obtained as discussed above. The results were corrected using (24) to give an indication of the error. The comparison of t_{EI}^0 and t_{MM}^0 to t_{MN}^0 is particularly interesting since these three methods are all zero order. Of these three methods t_{EI}^0 is much worse than the other two. Table IV compares some of the methods as a function of the number of square-integrable basis functions. At the energy shown (and at other energies we have examined) t_{EI}^0 converges poorly whereas t_{MM}^0 converges very well. It is interesting that t_{EI}^K is often accurate when t_{EI}^0 is very inaccurate.

Table IV shows that in general the variationally corrected results converge much faster than the zero-order results. However, all the methods except the Euler integral method yield tangents that converge to within 7×10^{-5} of the exact tangent of the phase shift at $n = 14$ (not shown in table).

It is of interest to compare the Born approximation results with the results obtained by the algebraic variational methods with $n = 0$. The Born approximation uses the trial function $S_i(r)$. Thus $t_B^0 = 0$ and the Born approximation result t_B^K is computed from the one integral M_{SS} . At $k = 0.55a_0^{-1}$, this method yields $t_B^K = 0.99547511$. The table shows that all the other methods, even with $n = 0$ are superior to the Born approximation. In comparison of the computational effort required note that the Born approximation requires the evaluation of one free-free integral, the zero-order Kohn method requires two, and the variationally corrected Kohn method requires four. With $n = 0$, the algebraic variational methods are much more sensitive to the choice of $C_i(r)$ than with large n . As n is increased the choice of $C_i(r)$ becomes less important.

As the size of the basis set is increased the widths of the regions affected by spurious singularities become smaller and eventually go to zero in the limit $n \rightarrow \infty$. At any given energy the calculations eventually (as n is increased) converge monotonically (a bound principle becomes applicable) to the exact answer. These and other details about bounds and convergence may be found elsewhere.^{31,43,58-65}

I. The Optimized Anomaly-Free Method

One possible difficulty with the anomaly-free method was pointed out in Section II.H. Another difficulty is that the calculated phase shifts are not continuous functions of energy or of changes in the parameters in

the basis set. Nesbet and Oberoi^{48,49} have proposed a method they call the optimized anomaly-free method which is supposed to cure some of the difficulties of the anomaly-free method. It is formulated in such a way that it gives no pseudoresonances and no pseudoantiresonances. Some results computed by their formulas are included in Tables I through IV as t_{0AF} .

J. The Minimum Variance Method and the Least-Squares Method

Recently Bardsley et al.⁶⁵ have proposed calculations based on minimization of the variance integral

$$U(X_i^0) = \int_0^\infty dr |w(r)L_i X_i^0(r)|^2 \quad (157)$$

or the variance sum

$$U_R(X_i^0) = \sum_i |w(r_i)L_i X_i^0(r_i)|^2 \quad (158)$$

where $w(r)$ is an arbitrary weighting function. Earlier Miller⁶⁶ had considered (157) with the special choice $w(r) = 1$. $U(X_i^0)$ and $U_R(X_i^0)$ are nonnegative; these schemes have the advantage of containing an internal criterion by which one can choose between two different basis sets used for X_i^0 , that is, one chooses whichever of the two basis sets leads to a lower value of $U(X_i^0)$ or $U_R(X_i^0)$. The minimum-norm method also has this ability to choose between two different basis sets; that is, one chooses the basis set that yields the lowest eigenvalue of the matrix Q . The methods of the Kohn and Rubinow type also have a criterion for choosing between basis sets; that is, one chooses the basis set for which $|\text{DET } M|$ is smaller, or for which the variational correction to the phase shift is smaller. This criterion, however, is not quite as satisfying as the criterion of minimum variance or of minimum eigenvalues of the matrix Q since the latter converge monotonically as additional basis functions are added but $|\text{DET } M|$ and the corrections to the phase shift do not.

Ládanyi et al.⁶³ have considered a generalization of the method of moments based on use of the trial function

$$X_i^0(r) = \alpha_{i0} S_i(r) + \alpha_{i1} C_i(r) + \sum_{a=1}^n c_a^i \eta_a^i(r) \quad (159)$$

with

$$(\alpha_{i0}^0)^2 + (\alpha_{i1}^0)^2 = 1 \quad (160)$$

and minimization of

$$\lambda(X_i^0) = \sum_{i=0}^{k>n} \left| \int_0^\infty dr w_i(r) L_i X_i^0(r) \right|^2 \quad (161)$$

They call this the least-squares method. This method has a number of features in common with the method of minimization of the variance integral.

K. Methods Involving Artificial Channel Radii

Another way to do scattering calculations by expanding the wave function in basis functions is to divide all space into an internal region and an external region. The wave function is expanded in a set of square-integrable basis functions in the internal region ($r < a$, where a is the so-called "channel radius") and in terms of functions like S_l and C_l in the external region ($r > a$). The boundary is chosen so that the potential is zero or simple for $r > a$. Thus the difficult part is to solve for the wave function in the internal region, and for this part we can use techniques similar to those used in bound-state problems. Eventually the solutions in the internal and the external region are matched. Techniques that incorporate such an artificial "channel radius" are very popular in nuclear physics and are here called artificial channel radius theories.

The oldest of the artificial channel radius theories is the theory of Kapur and Peierls.⁶⁷ The most popular of the artificial channel radius theories is the derivative matrix technique of Wigner and Eisenbud.⁶⁸ The derivative matrix is often called the R matrix (it should not be confused with the reactance or reaction matrices; to avoid this confusion we call it the NR matrix). For single-channel scattering it is a 1×1 matrix (i.e., a number).

In the derivative matrix method one uses in the internal region the set of n basis functions $\mu_{ij}(r)$ which have been orthonormalized as follows

$$\int_0^a dr \mu_{ii}(r) \mu_{ij}(r) = \delta_{ij} \quad i, j = 1, 2, \dots, n \quad (162)$$

and which satisfy the boundary conditions

$$\mu_{ij}(0) = 0 \quad j = 1, 2, \dots, n \quad (163)$$

$$\frac{a}{\mu_{ij}(a)} \frac{d\mu_{ij}}{dr} \Big|_{r=a} = b \quad j = 1, 2, \dots, n \quad (164)$$

where b is a constant.

Then one diagonalizes the matrix $H^{\mu\mu l}$ where

$$H_{ij}^{\mu\mu l} = \int_0^a dr \mu_{ii}(r) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right] \mu_{ij}(r) \quad (165)$$

to obtain the eigenfunctions

$$w_{ik}(r) = \sum_j c_{ijk} \mu_{ij}(r) \quad (166)$$

and eigenvalues E_{ik} . Note the diagonalization must be done only once, not at every energy. The solution at given energy is expanded in the internal region as

$$X_i^0(r) = \sum_k A_k w_{ik}(r) \quad (167)$$

where we have suppressed a subscript l on A_k . To determine the coefficients we require

$$\int_0^a dr \mu_{ij}(r) L_i X_i^0(r) = 0 \quad j = 1, 2, \dots, n \quad (168)$$

which, using integration-by-parts twice and (165) through (167), yields

$$X_i^0(a) = NR \left[a \frac{dX_i^0}{dr} \Big|_{r=a} - b X_i^0(a) \right] \quad (169)$$

where NR is the element of the derivative matrix and is given by

$$NR = \left(\frac{\hbar^2}{2ma} \right) \sum_{k=1}^n \frac{[w_{ik}(a)]^2}{E_{ik} - E} \quad (170)$$

The most common practice in derivative matrix theory is to use in the external region a linear combination of an incoming wave $I_i(r)$ and an outgoing wave $O_i(r)$ satisfying complex boundary conditions. However, the theory has also been stated in terms of the more convenient functions satisfying boundary conditions like (43) and (44). Thus we assume that in the external region

$$X_i^0(r) = \mathcal{S}_i(r) + t_i^0 \mathcal{C}_i(r) \quad (171)$$

where $\mathcal{S}_i(r)$ and $\mathcal{C}_i(r)$ have the asymptotic forms

$$\mathcal{S}_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r j_i(kr) \quad (172)$$

$$\mathcal{C}_i(r) \underset{r \rightarrow \infty}{\sim} a_0^{-1/2} k r \xi_i(kr) \quad (173)$$

and in addition satisfy

$$L_i \mathcal{S}_i = 0 \quad (174)$$

$$L_i \mathcal{C}_i = 0 \quad (175)$$

in the external region. Comparing (171) to (169) yields

$$\begin{aligned} & \mathcal{S}_i(a) - NR \left[a \frac{d\mathcal{S}_i}{dr} \Big|_{r=a} - b \mathcal{S}_i(a) \right] \\ & + t_i^0 \left\{ \mathcal{C}_i(a) - NR \left[a \frac{d\mathcal{C}_i}{dr} \Big|_{r=a} - b \mathcal{C}_i(a) \right] \right\} = 0 \quad (176) \end{aligned}$$

which can be solved for t_i^0 . The derivative matrix method has the advantage of requiring no free-free integrals but the disadvantage that the square-integrable basis will probably have to be very large. This disadvantage results from the fact that the square-integrable basis must be used to expand the scattering wave function in the whole internal region but the channel radius may have to be large.

An alternative method of derivation of the derivative matrix method can be given^{49,69} which shows that the variational correction to t_i^0 computed from (176) vanishes and that t_i^0 is stationary with respect to variation of the coefficients in the trial wave function. These properties are not obvious in the usual type of derivation (such as given above).

However, the derivative matrix method still has an important disadvantage,^{49,69,70} namely, that the wave function has a discontinuous derivative at the channel radius. The method converges to the correct answer and the discontinuity vanishes as the number of basis functions is increased but in practical calculations the finite discontinuity in the derivative is undesirable.

A method that has a number of the derivative matrix method's advantages, including division into internal and external regions and variationally correct results, has been proposed by Crawford.⁷¹ Crawford uses an analogue of the Kohn variational theory in which the surface terms in the derivation of the variational expression are calculated at a finite channel radius rather than in the asymptotic limit.⁶⁹ In this method in the external region we write

$$X_i^0(r) = \left(\frac{ma_0}{\hbar k}\right)^{1/2} [\alpha_{i0}^0 \mathcal{S}_i(r) + \alpha_{i1}^0 \mathcal{G}_i(r)] \quad (177)$$

where $\mathcal{S}_i(r)$ and $\mathcal{G}_i(r)$ are defined by (172) to (175). Note that the $X_i^0(r)$ of (177) has different units from all our previous $X_i^0(r)$ and that

$$t_i^0 = \frac{\alpha_{i1}^0}{\alpha_{i0}^0} \quad (178)$$

Then the expression

$$\left(\frac{\hbar}{2}\right) \alpha_{i0}^0 t_i \alpha_{i0}^0 = -J(X_i^0) + \left(\frac{\hbar}{2}\right) \alpha_{i0} \alpha_{i1}^0 \quad (179)$$

where

$$J(X_i^0) = \int_0^a dr X_i^0(r) L_r X_i^0(r) \quad (180)$$

is stationary under a variation that preserves α_{i0} , that is,

$$\frac{\partial t_i}{\partial \alpha_{i1}^0} = 0 \quad (181)$$

Note that (178) and (179) are equivalent to (24) except that we have changed the normalization. In the interior region we expand

$$X_i^0(r) = \sum_i c_i \eta_i(r) \quad (182)$$

Now we require continuity of the trial function and its first derivative at $r = a$, that is,

$$\left(\frac{ma_0}{\hbar k}\right)^{1/2} [\alpha_{i0}^0 \mathcal{S}_i(a) + \alpha_{i1}^0 \mathcal{C}_i(a)] = \sum_i c_i \eta_i(a) \quad (183)$$

$$\left(\frac{ma_0}{\hbar k}\right)^{1/2} \left[\alpha_{i0}^0 \frac{d\mathcal{S}_i}{dr} \Big|_{r=a} + \alpha_{i1}^0 \frac{d\mathcal{C}_i}{dr} \Big|_{r=a} \right] = \sum_i c_i \frac{d\eta_i}{dr} \Big|_{r=a} \quad (184)$$

These two equations can be solved for

$$\alpha_{i0}^0 = \sum_i \beta_{i0i} c_i \quad (185)$$

and

$$\alpha_{i1}^0 = \sum_i \beta_{i1i} c_i \quad (186)$$

where

$$\beta_{i0i} = -\left(\frac{\hbar}{kma_0}\right)^{1/2} \left[\frac{d\mathcal{C}_i}{dr} \eta_i(r) - \mathcal{C}_i(r) \frac{d\eta_i}{dr} \right] \Big|_{r=a} \quad (187)$$

and

$$\beta_{i1i} = \left(\frac{\hbar}{kma_0}\right)^{1/2} \left[\frac{d\mathcal{S}_i}{dr} \eta_i(r) - \mathcal{S}_i(r) \frac{d\eta_i}{dr} \right] \Big|_{r=a} \quad (188)$$

In deriving this result we use the constancy of the Wronskian of the external solutions $\mathcal{S}_i(r)$ and $\mathcal{C}_i(r)$, that is,

$$\mathcal{S}_i(r) \frac{d\mathcal{C}_i}{dr} - \frac{d\mathcal{S}_i}{dr} \mathcal{C}_i(r) = -k \quad (189)$$

We can rewrite (185) and (186) using the row vectors β_{i0} and β_{i1} and the column vector \mathbf{c} as

$$\alpha_{i0}^0 = \beta_{i0} \mathbf{c} \quad (190)$$

$$\alpha_{i1}^0 = \beta_{i1} \mathbf{c} \quad (191)$$

Then we can write the stationary expression as

$$\sum_{ij} \beta_{i0i} c_i t_{ij} \beta_{j0j} c_j = -\left(\frac{2}{\hbar}\right) \sum_{ij} c_i c_j L_{ij}^{nn} + \sum_{ij} \beta_{i0i} c_i \beta_{j1j} c_j \quad (192)$$

where

$$L_{ij}^{nn} = \int_0^a dr \eta_i^*(r) L_i \eta_j(r) \quad (193)$$

The matrix equivalent of the stationary expression is thus

$$\mathbf{c}^\dagger \beta_{i0}^\dagger t_i \beta_{i0} \mathbf{c} = \mathbf{c}^\dagger \mathbf{B} \mathbf{c} \quad (194)$$

where the dagger indicates the transpose matrix and

$$\mathbf{B} = -\left(\frac{2}{\hbar}\right) \mathbf{L}^{in} + \beta_{i0}^\dagger \beta_{i1} \quad (195)$$

The stationary value of t is given by (194) when the coefficients c_i are such that the right-hand side is stationary with respect to all variations of c_i subject to the constraint $\alpha_{i0}^0 = \sum_i \beta_{i0} c_i$. Thus we introduce a Lagrange multiplier λ and consider

$$J'(X_i^0) = \mathbf{c}^\dagger \mathbf{B} \mathbf{c} + \lambda \beta_{i0} \mathbf{c} \quad (196)$$

Requiring

$$\frac{\partial J'(X_i^0)}{\partial c_i} = 0 \quad (197)$$

yields

$$\mathbf{c}^\dagger \mathbf{B} = -\lambda \beta_{i0} \quad (198)$$

that is,

$$\mathbf{B}^\dagger \mathbf{c} = -\lambda \beta_{i0}^\dagger \quad (199)$$

that is,

$$\mathbf{c} = -\lambda (\mathbf{B}^\dagger)^{-1} \beta_{i0}^\dagger \quad (200)$$

Assuming \mathbf{B} is symmetric we then find that the stationary value of t satisfies

$$t_i \beta_{i0}^\dagger \beta_{i0} = \mathbf{B} \quad (201)$$

That is,

$$t_i = (\beta_{i0} \mathbf{B}^{-1} \beta_{i0}^\dagger)^{-1} \quad (202)$$

Using (190) and (200), that is,

$$\alpha_{i0}^0 = (-\lambda) \beta_{i0} (\mathbf{B}^{-1}) \beta_{i0}^\dagger \quad (203a)$$

$$= (-\lambda) t_i^{-1} \quad (203b)$$

we find $\lambda = -t_i \alpha_{i0}^0$. (Thus we can find λ for any choice of the arbitrary α_{i0}^0 .) This method will be called the Kohn-Crawford procedure.

Oberoi and Nesbet⁷² have suggested a modification of the Kohn and Rubinow methods in which the functions $S_i(r)$ and $C_i(r)$ are replaced by $\mathcal{S}_i(r)$ and $\mathcal{C}_i(r)$, respectively, for $r \geq a$. Oberoi and Nesbet call these functions numerical asymptotic functions. The functions are still to be arbitrary at small r except for the zero value at the origin. This procedure simplifies the free-free and bound-free integrals and has similar advantages to the Kohn-Crawford procedure.

L. Methods Involving Only Square-Integrable Basis Functions but No Artificial Channel Radii

There are many approaches to the treatment of resonances in which one approximates the scattering wave function in the resonance energy region by a square-integrable function. Recently some methods have been proposed for treating scattering problems in resonant or nonresonant energy regions by doing calculations involving only square-integrable basis functions. Schlessinger and Schwartz⁷³ proposed solving the scattering problem by solving a nonhomogeneous modification of (3) for negative energies and using rational fractions to extrapolate the partial wave contribution to the scattering amplitude to positive energies.

Reinhardt and co-workers⁷⁴ have proposed that a square-integrable basis set be used to calculate the Fredholm determinant for complex E and that rational fractions be used to extrapolate it to the real axis. The phase shift can be calculated from the extrapolated determinant. This method is closely related to the methods of Schlessinger and Schwartz, but appears to have some advantages. Doolen *et al.*⁷⁵ have proposed yet another way to use complex variable analyticity to calculate scattering amplitudes, namely the rotation method involving complex coordinates and complex energies.

M. The Schwinger Variational Method

Another of the standard variational methods of scattering theory which can be applied using basis functions is the Schwinger variational method.^{76,77} This method can be used in an algebraic variational calculation with a trial function of the form (40) or with a trial function that does not even satisfy correct scattering boundary conditions, for example, a power series.⁷⁸ It has the disadvantage that it requires more complicated integrals than any of the methods discussed so far; that is, it requires integrals involving the Green's function. This is the reason it has received less attention. Kato³⁷ and Schwartz⁷⁹ have given different methods for eliminating the integrals involving the Green's function. Kato's method introduces different complicated integrals and Schwartz's method involves a special choice of trial function. Overall, the Schwinger method still appears to be less well suited to algebraic variational calculations than the methods considered above.

N. Other Methods

Malik⁵¹ has introduced a variational method that is identical to the Kohn method except that (49) is replaced by

$$t_i^0 = - \frac{2ma_0^{1/2}}{\hbar^2 k} \int_0^\infty dr X_i^0(r) L_i(kr)^{-1} j_i(kr) \quad (204)$$

John⁴² has considered methods in which various new combinations of $n + 1$ of the sets of $n + 3$ equations (48), (50b), (49) or (54), and (204) are used. Calculations⁴² indicate these methods are generally in good agreement with the Kohn, Rubinow, and Hulthén methods.

Knudson and Kirtman⁸⁰ have presented a variation-perturbation treatment of scattering in which the Hulthén method is used to obtain X_1^0 . This causes the first-order correction to the phase shift to vanish (as discussed above). Knudson and Kirtman consider the second- and third-order corrections to the phase shift.

Kohn⁸¹ has considered the scattering variational principle in momentum space.

III. MULTICHANNEL SCATTERING

A. Introduction

For scattering of composite particles we use multichannel scattering theory. For such problems we must determine the dependence of the wave function both on the internal coordinates of the composite particles and also on the coordinates that describe their relative motion. These two dependencies are coupled. Most of the variational methods for central potential scattering discussed in Sections II.C, II.D, and II.F through II.N can be extended to treat the relative motion part of the multichannel scattering problem, and many have been so extended. Coupling each of these treatments to the former part of the problem (i.e., with the treatment of the internal motion) can be done in a large variety of ways, leading to an even larger number of ways in which the combined problem can be solved. Many of the earliest treatments considered only special choices of trial function or considered only special cases, for example, problems involving only two channels. In this section we consider some of the more general and systematic formalisms that can be applied in a straightforward way to a large number of multichannel scattering processes. (The very earliest work on multichannel algebraic variational scattering calculations in chemical physics was carried out by Huang⁸ and Massey and Moiseiwitsch.³⁷ In these calculations only one channel is open. Massey and Moiseiwitsch^{82,83} were the first to treat a case in which more than one channel is open. Reviews of the early work were provided by Huck⁸⁴ and Mott and Massey.⁸⁵)

B. Wave Functions and Kohn, Rubinow, Minimum-Norm, and Anomaly-Free Methods

The wave function is expanded in eigenfunctions of total angular momentum, and (as in single-channel scattering) each total angular momentum may be considered separately. In a multichannel scattering

calculation with N open two-body channels of a given total angular momentum, the component of the wave function with that total angular momentum has the asymptotic property (we restrict ourselves to the case where there are no open three-body channels)

$$\psi^p \sim \sum_{i=1}^N Y_{ip}(r_i) f_i(x_i) \quad (205)$$

where

$$Y_{ip}(r_i) \equiv \alpha_{0ip} A_{i0}(r_i) + \alpha_{1ip} A_{i1}(r_i) \quad (206)$$

$$H_i(x_i) f_i(x_i) = E_i f_i(x_i) \quad (207)$$

and the channel Hamiltonians H_i are defined in terms of the total Hamiltonian H by

$$H_i(x_i) = \lim_{r_i \rightarrow \infty} [H(r_i, x_i) - T(r_i)] \quad (208)$$

where $T(r_i)$ is the kinetic energy of relative motion in channel i . In channel i , r_i is the radial coordinate of relative motion of the two subsystems, x_i denotes the collection of the remaining coordinates in the barycentric Hamiltonian in that channel, and $f_i(x_i)$ are the eigenfunctions of $H_i(x_i)$, that is, the "internal eigenfunctions." The "free functions" A_{i0} and A_{i1} have the asymptotic properties

$$A_{i0}(r_i) \sim_{r_i \rightarrow \infty} r_i^{-1} a_0^{-1/2} \sin \theta_i \quad (209)$$

$$A_{i1}(r_i) \sim_{r_i \rightarrow \infty} r_i^{-1} a_0^{-1/2} \cos \theta_i \quad (210)$$

where

$$\theta_i = k_i r_i - \frac{1}{2} l_i \pi - v_i \ln 2k_i r_i + \sigma_i \quad (211)$$

l_i is the orbital angular momentum of relative motion in channel i , k_i is the wave number wave in channel i , that is,

$$k_i = \hbar^{-1} \mu_i v_i \quad (212)$$

μ_i is the reduced mass, and v_i is the velocity for relative motion in channel i , that is,

$$v_i = \left[\frac{2(E - E_i)}{\mu_i} \right]^{1/2} \quad (213)$$

$$v_i = \frac{Z_{A_i} Z_{B_i}}{k_i} \quad (214)$$

Z_{A_i} and Z_{B_i} are the charges on the subsystems in channel i , and

$$\sigma_{i_i} = \arg \Gamma(l_i + 1 + i v_i) \quad (215)$$

[Sometimes it is convenient to add a factor of $v_i^{-1/2}$ to the right-hand sides of (209) and (210). We do not do that in this article.] The problem is to

approximate solutions to the Schrödinger equation with boundary conditions (205) and to examine the Y_{im} to find $\{\alpha_{\beta im}\}$. From the latter quantities we can find the approximate reactance matrix and hence the approximate cross-sections. By using numerical techniques we attempt to make the differences from the exact reactance matrix elements and cross-sections as small as desired.

One approach to solving this problem is the eigenfunction-expansion method (also called the coupled-channels method or the close-coupling method). In this approach the wave function is expanded as

$$\psi^0 = \sum_{i=1}^P X_{ip}^0(r_i) f_i(x_i) \quad (216)$$

where

$$X_{ip}^0(r_i) \underset{r_i \rightarrow \infty}{\sim} Y_{ip}^0(r_i) \quad (217)$$

or $X_{ip}^0(r_i)$ may be square-integrable. The superscript 0 indicates a trial value or a quantity appearing in a trial function. Coupled differential equations⁸⁶⁻¹⁰⁷

$$\sum_{j=1}^P [H_{ij}^{op} - E \delta_{ij}] X_{jp}^0(r_j) = 0 \quad i = 1, 2, \dots, P \quad (218)$$

$$H_{ij}^{op} \equiv \int dx_i f_i(x_i) H(r_i, r_i) f_j(x_j) \quad (218a)$$

for the X_{jp}^0 are derived by requiring that $(H - E)\psi^0$ have no component in the space spanned by the $\{f_i(x_i)\}_1^P$. The same differential equations may be derived by considering the *Kohn variational functional*^{6,14,26}

$$I_{pq} \equiv \langle \psi^0 | H - E | \psi^0 \rangle \quad (219)$$

and using the *Kohn variational principle* for the reactance matrix elements to require that there be no first-order corrections to the approximate reactance matrix elements under point-by-point variation of the $X_{ip}^0(r_i)$. In the case where rearrangement channels are included in the expansion (216), that is, when all r_i are not the same, the differential equations become integrodifferential equations. If the set of eigenstates of H_i included in the trial wave function expansion includes at least all the open channels, then the minimum principles^{59,108,109} first developed by Spruch and co-workers may be applied. In the most useful version of these principles, one proves that the sum of the eigenphase shifts increases monotonically as the basis set is increased. Notice the difference of this minimum principle from the bound principles of single-channel scattering. In single-channel scattering we are concerned with bounding errors caused by approximations to the continuum wave function $X_i(r)$. To use the

Spruch-type minimum principle, however, we must solve for the continuum functions $X_{j,p}(r_j)$ by essentially exact numerical techniques and one is concerned with errors caused by approximating the target part of the wave function. In algebraic variational methods we desire to avoid the numerical integration of (coupled integro) differential equations and thus the Spruch-type minimum principle is not directly applicable. We return to this point in Section III.E below.

Note that for scattering processes involving identical particles all the $\alpha_{\beta i p}$ are not independent. If channel j is related to channel i by a permutation of identical particles then $\alpha_{\beta j p} = \pm \alpha_{\beta i p}$. Thus for example, in electron-hydrogen atom scattering where we may assume the nucleus is infinitely heavy so $r_2 = x_1$ and $r_1 = x_2$, we use $(1 \pm P_{12}) \sum_{i=1}^N X_{i p}^0(r_1) f_i(r_2)$ where the permutation operator P_{12} interchanges r_1 and r_2 rather than using $\sum_{i=1}^N [X_{i p}^0(r_1) f_i(r_2) + X_{N+i, p}^0(r_2) f_i(r_1)]$. In this way we include all the arrangement channels but do not increase the number of independent coefficients $\alpha_{\beta i p}$. In a similar way (for any scattering problem) we can multiply any trial wave function considered in this section by a projection operator or permutation operator to enforce correct permutational symmetry.¹¹¹ We do not include these operators explicitly in the equations but it can be done when necessary.

In general, the number P of open channels included in the trial wave function expansion must be equal to or larger than the number N of open channels for the expansion (216) to yield an accurate approximation. In some cases, especially where rearrangements are possible, letting the expansion (216) include all square-integrable internal eigenfunctions of all two-body channel Hamiltonians does not yield an accurate approximation. Rather than include continuum internal eigenfunctions in (216) which leads to difficulties in satisfying the scattering boundary conditions,¹¹⁰ two alternative approaches have been used. One approach¹¹²⁻¹¹⁵ is to add terms of the form $Z_{j,p}(r_j) g_j(x_j)$ to the expansion where g_j are square-integrable but are not eigenfunctions of H_j and are not necessarily linear combinations of square-integrable eigenfunctions of H_j . These states are called pseudostates. The other approach, the correlation method¹¹⁶⁻¹²¹ of Gailitis, Burke and Taylor, and Miller, is to use an expansion of the form

$$\psi^0 = \sum_{i=1}^P X_{i p}^0(r_i) f_i(x_i) + \sum_{m=1}^M c_{m p} W_m(r_i, x_i) \quad (220)$$

where the $W_m(r_i, x_i)$ are square-integrable functions added to make the basis set complete. The $W_m(r_i, x_i)$ are called correlation functions. Miller¹²⁰ and Hahn¹²² showed how to use a trial function like (220) to treat

rigorously rearrangements of particles with arbitrary masses without using projection operators. (Their procedures are incorporated into Sections III.C and III.D below.) Note that the two sums in (220) are not orthogonal. Requiring that $(H - E)\psi^0$ have no component in the spaces spanned by the $\{f_i\}$ and the $\{W_m\}$, we can derive a set of coupled algebraic and (integro) differential equations for the c_{mp} and $X_{ip}^0(r_i)$. Using projection operator techniques¹²³ we can derive an exactly equivalent set of equations in which the effect of the correlation functions is merely to add extra nonlocal potential matrix elements to the H_{ij} in (218) for the $X_{ip}^0(r_i)$. The same (integro) differential equations, containing the extra potential terms, for the $X_{ip}^0(r_i)$ may be derived by considering the *Kohn variational functional* (219) and using the *Kohn variational principle* for the reactance matrix elements to require that there be no first-order corrections²⁸ to the approximate reactance matrix elements under point-by-point variation of the $X_{ip}^0(r_i)$ and variation of the coefficients c_{mp} . When at least all the open channels are included in the sum over i in (220), it can be called the generalized variational bound method because of the minimum principle which is then satisfied.^{116-120,122}

The Hulthén, Kohn, and Harris algebraic variational methods of potential scattering theory were extended to elastic scattering of composite particles using a trial function like^{10,11,37,38,39,124-127}

$$\psi^0 = Y_{1p}^0(r_i)f_1(x_i) + \sum_{m=1}^M c_{mp}W_m(r_i, x_i) \quad (221)$$

We next consider algebraic variational methods that may be systematically applied to elastic and inelastic scattering.

Harris and Michels^{15,16} have considered a trial function of a form closely related to (220). They considered the trial function

$$\psi^0 = \sum_{i=1}^P Y_{ip}^0(r_i)f_i(x_i) + \sum_{m=1}^M c_{mp}W_m(r_i, x_i) \quad (222)$$

and they specifically chose the first sum in (222) to be orthogonalized to the second sum. Whereas in (220) the $X_{ip}(r_i)$ are subjected to point-by-point variation, in (222) the $Y_{ip}(r_i)$ may be varied only in the sense of using various coefficients α_{0ip} , α_{1ip} [see (206)]. Harris and Michels solve for trial-function values of α_{0ip} , α_{1ip} , and c_{mp} by requiring that $(H - E)\psi^0$ have no component in the space spanned by the $\{W_m(r_i, x_i)\}_1^M$ and by minimizing the components of $(H - E)\psi^0$ in the spaces spanned by the $\{A_{i0}(r_i)f_i(x_i)\}_1^P$ and the $\{A_{i1}(r_i)f_i(x_i)\}_1^P$. Thus this part of their procedure is a least-squares method in the general sense of the term. Then they substitute this trial function into the Kohn or Rubinow variational

principle for the reactance matrix elements to obtain improved estimates¹²⁸ of the α_{0ip} and α_{1ip} . In Section III.C we illustrate multichannel algebraic variational techniques by using the Kohn and Rubinow variational methods^{6,14} to solve for the coefficients in the trial function (222). Then we substitute the trial function into the Kohn and Rubinow variational principle^{6,14} for the reactance matrix elements and the reciprocals of the reactance matrix elements, respectively, to obtain improved estimates of the α_{0ip} and α_{1ip} . A further difference in Section III.C as compared to Harris and Michels' work is that we do not require orthogonality in the two sums (see also Appendix 1). The procedure of Section III.C is applicable to both nonrearrangements and rearrangements.

Recently Nesbet¹⁴ considered conversion of the close-coupling method including only open channels [see (216)–(218)] from a problem in coupled differential or integrodifferential equations to an algebraic problem by rewriting the trial function (216) as

$$\psi^{p^0} = \sum_{i=1}^P \left[Y_{ip}^0(r_i) + \sum_{a=1}^{n_i} c_{ap}^i \eta_a^i(r_i) \right] f_i(x_i) \quad (223)$$

Then the point-by-point variation of the functions $X_{ip}^0(r_i)$ is replaced by the variation of the coefficients c_{ap}^i , α_{0ip}^0 , and α_{1ip}^0 . Nesbet used the Kohn, Rubinow, and anomaly-free variational methods to solve for the coefficients in the trial function (223). He then used the Kohn, Rubinow, and anomaly-free variational principles to determine improved values of α_{0ip} and α_{1ip} . Note that the anomaly-free method is just a choice between the Kohn and Rubinow methods based upon a criterion given by Nesbet. This type of treatment was extended easily¹⁷ to include closed channels, that is, to use the trial function

$$\psi^{p^0} = \sum_{i=1}^P Y_{ip}^0(r_i) f_i(x_i) + \sum_{i=1}^Q \sum_{a=1}^{n_i} c_{ap}^i \eta_a^i(r_i) f_i(x_i) \quad (224)$$

where $Q > P$. In Section III.D we consider the conversion of the correlation method for nonrearrangement or rearrangement scattering [see (220)] from a problem of coupled differential or integrodifferential equations to an algebraic problem using the Kohn, Rubinow, and anomaly-free variational methods. The extension of these variational methods to a correlation-type trial function has also been considered by Nesbet and Lyons¹²⁹ and Chung and Chen.^{130,131}

The above discussion and references should make it clear that the methods presented in Sections III.C and III.D depend especially on the earlier developments of Gailitis, Burke and Taylor, Miller, Harris and Michels, and Nesbet.

C. Application of the Kohn Variational Method to the Harris and Michels-type Trial Function

We first consider the case where

$$\alpha_{0ip} = \alpha_{0ip}^0 = \delta_{ip} \quad i, p = 1, 2, \dots, P \quad (225)$$

where the first quantity is the exact value of α_{0ip} and the second is the trial value of α_{0ip} . Then by the definition of the reactance matrix, it is given by¹³²

$$\mathbf{R} = \mathbf{V}^{1/2} \alpha_1 \mathbf{V}^{-1/2} \quad (226a)$$

or

$$R_{ij} = \left(\frac{v_i}{v_j} \right)^{1/2} \alpha_{1ij} \quad i, j = 1, 2, \dots, P \quad (226b)$$

where $V_{ij} \equiv v_i \delta_{ij}$. Note that i is the final channel and j is the initial channel. Since the reactance matrix is real, we restrict α_{1ij} to real values. We now consider the variational determination of the coefficients α_{1ip}^0 and c_{mp} in the trial function given by (222), (206), and (225). Under variation of all the α_{1ip} , α_{1iq} , c_{mp} , and c_{mq} ($i = 1, 2, \dots, P$; $m = 1, 2, \dots, M$), the *Kohn variational principle* for the reactance matrix elements in the form in which it is commonly used (see, for example, Refs. 91, 97, 117, 119, and 15) is

$$\delta \left[I_{pq} - \left(\frac{\hbar v_p}{2a_0} \right) \alpha_{1pq}^0 \right] = 0 \quad p, q = 1, 2, \dots, P \quad (227)$$

That is, the stationary value of α_{1pq} is

$$\alpha_{1pq}^1 = \alpha_{1pq}^0 - \left(\frac{2a_0}{\hbar v_p} \right) (I_{pq}) \quad (228)$$

where the superscripts 1 and 0 denote variationally corrected and trial values, respectively. In the methods using point-by-point variation (functional variation) of the $X_{ip}^0(r_i)$ one sets I_{pq} equal to 0 by requiring the $X_{ip}^0(r_i)$ to satisfy (integro) differential equations.^{91,97,117,119,120} For example, if the trial function is (216), the (integro) differential equations are (218).^{91,97} In that case α_{1pq}^1 equals α_{1pq}^0 ; that is, the variationally correct reactance matrix elements are given directly by the asymptotic form of the trial function. In the algebraic variational methods, such as the one considered here, we do not make the correction to the trial reactance matrix elements vanish completely. Following the Kohn variation method we note that the stationary condition (227) is satisfied with respect to the restricted functional form of the trial function when

$$\frac{\partial I_{pq}}{\partial c_{mr}} = 0 \quad \begin{array}{l} r = p, q \\ p, q = 1, 2, \dots, P \\ m = 1, 2, \dots, M \end{array} \quad (229)$$

and when

$$\frac{\partial I_{pq}}{\partial \alpha_{ij}^0} = \frac{\hbar v_i}{2a_0} (\delta_{ip} \delta_{jq}) \quad \begin{matrix} i, p, q = 1, 2, \dots, P \\ j = p, q \end{matrix} \quad (230)$$

Using these equations to determine values for the parameters α_{1pq}^0 , we can then use (228) to obtain an improved approximation. The use of (229) and (230) to obtain values of a particular coefficient α_{1pq}^0 proceeds as follows:

$$I_{pq} = I_{pq}^{FF} + I_{pq}^{CF} + I_{pq}^{CF*} + I_{pq}^{CC} \quad (231)$$

where

$$I_{pq}^{FF} = \sum_{ij} \langle Y_{ip}^0 f_i | H - E | Y_{jq}^0 f_j \rangle \quad (232)$$

$$I_{pq}^{CF} = \sum_{mi} c_{mp}^* \langle W_m | H - E | Y_{iq}^0 f_i \rangle \quad (233)$$

$$I_{pq}^{CC} = \sum_{mn} c_{mp}^* c_{nq} \langle W_m | H - E | W_n \rangle \quad (234)$$

Then requiring $\partial I_{pq} / \partial c_{mp}^* = 0$ yields

$$\sum_n \langle W_m | E - H | W_n \rangle c_{nq} = \sum_i \langle W_m | H - E | Y_{iq}^0 f_i \rangle \quad (235)$$

$$\begin{matrix} m = 1, 2, \dots, M \\ q = 1, 2, \dots, P \end{matrix}$$

Or in a more compact notation,

$$I_{pq}^{CF} = \sum_m c_{mp}^* J_{mq} \quad (236)$$

$$I_{pq}^{CC} = -\sum_{mn} c_{mp}^* c_{nq} N_{mn} \quad (237)$$

where

$$J_{mq} \equiv \sum_i \langle W_m | H - E | Y_{iq}^0 f_i \rangle \quad (238)$$

and

$$N_{mn} \equiv \langle W_m | E - H | W_n \rangle \quad (239)$$

Then requiring $\partial I_{pq} / \partial c_{mp}^* = 0$ yields

$$\sum_n N_{mn} c_{nq} = J_{mq} \quad \begin{matrix} m = 1, 2, \dots, M \\ q = 1, 2, \dots, P \end{matrix} \quad (240)$$

or

$$\mathbf{c} = \mathbf{N}^{-1} \mathbf{J} \quad (241)$$

Notice that, although we obtained (240) by the Kohn variational principle, the result is the same as if we had arbitrarily required $(H - E)\psi^0$ to have no component in the space spanned by the $\{W_m\}$. Substituting (241) into

(231) yields

$$I_{pq} = I_{pq}^{FF} + \sum_m (N^{-1}J)_{mp}^* J_{mq} + \sum_m (N^{-1}J)_{mq} J_{mp}^* - \sum_{mn} (N^{-1}J)_{mp}^* (N^{-1}J)_{nq} N_{mn} \quad (242)$$

$$= I_{pq}^{FF} + 2 \sum_{mn} (N^{-1})_{mn}^* J_{np}^* J_{mq} - \sum_{mnor} (N^{-1})_{mo}^* J_{op}^* (N^{-1})_{nr} J_{rq} N_{mn} \quad (243)$$

Now the last term of (243) is equal to

$$- \sum_{mor} (N^{-1})_{mo}^* J_{op}^* \delta_{mr} J_{rq} \quad (244a)$$

$$= - \sum_{mo} (N^{-1})_{om} J_{op}^* J_{mq} \quad (244b)$$

Therefore,

$$I_{pq} = I_{pq}^{FF} + \sum_{mn} J_{np}^* (N^{-1})_{nm} J_{mq} \quad (245)$$

$$= \sum_{ij} \langle Y_{ip}^0 f_i | M | Y_{jq}^0 f_j \rangle \quad (246)$$

where

$$M = H - E - \sum_{mn} (H - E) |W_m\rangle \langle W_m| (H - E)^{-1} |W_n\rangle \langle W_n| (H - E) \quad (247)$$

Alternatively from (206), (225), and (246) we obtain

$$I_{pq} = M_{pq}^{00} + \sum_j M_{pj}^{01} \alpha_{1jq} + \sum_j \alpha_{1jp}^0 M_{jq}^{10} + \sum_{ij} \alpha_{1ip}^0 M_{ij}^{11} \alpha_{1jq}^0 \quad (248)$$

where

$$M_{ij}^{\alpha\beta} = \langle A_{i\alpha}^0 f_i | M | A_{j\beta}^0 f_j \rangle \quad (249)$$

with $\alpha, \beta = 0, 1$. Note that

$$\frac{\partial I_{pq}}{\partial \alpha_{1ij}^0} = \delta_{jp} \left(M_{iq}^{10} + \sum_k M_{ik}^{11} \alpha_{1kq}^0 \right) + \delta_{jq} \left(M_{pi}^{01} + \sum_k M_{ki}^{11} \alpha_{1kp}^0 \right) \quad (250)$$

Now (230) requires $\partial I_{pq} / \partial \alpha_{1ip}^0 = 0$ for $p \neq q$ which yields

$$\sum_k M_{ik}^{11} \alpha_{1kq}^0 = -M_{iq}^{10} \quad q \neq p \quad (251)$$

Further we include the case $p = q$ by using, again from (230):

$$\frac{\partial I_{pq}}{\partial \alpha_{1iq}^0} = \frac{\hbar v_i}{2a_0} \delta_{ip} \quad (252)$$

This yields

$$\delta_{pq} \left(M_{iq}^{10} + \sum_k M_{ik}^{11} \alpha_{1kq}^0 \right) + M_{pi}^{01} + \sum_k M_{ki}^{11} \alpha_{1kp}^0 = \left(\frac{\hbar v_i}{2a_0} \right) \delta_{ip} \quad (253)$$

But¹⁴

$$M_{pi}^{01} - M_{ip}^{10} = \left(\frac{\hbar v_i}{2a_0} \right) \delta_{ip} \quad (254)$$

and

$$M_{ki}^{11} = M_{ik}^{11} \quad (255)$$

Thus (231) becomes

$$(1 + \delta_{pq}) \left(M_{ip}^{10} + \sum_k M_{ik}^{11} \alpha_{kp}^0 \right) = 0 \quad (256)$$

Equation (256) is not different from (251) so we can write for all i and j :

$$\sum_k M_{ik}^{11} \alpha_{kj}^0 = -M_{ij}^{10} \quad (257)$$

or

$$\alpha_1^0 = -(\mathbf{M}^{11})^{-1} \mathbf{M}^{10} \quad (258)$$

This equation can be solved for the trial coefficients α_{iq}^0 . (These can be used with (206) and (241) to calculate the trial $\{c_{mp}\}$ if it is desired to use the trial wave functions. If one wants only to calculate the reactance and scattering matrices, then one need not explicitly obtain the $\{c_{mp}\}$.) Equation (258) may now be substituted into (248) to obtain

$$\mathbf{I} = \mathbf{M}^{00} + \mathbf{M}^{01} \alpha_1^0 \quad (259)$$

Now (258) and (259) can be used on the right-hand side of (228) to obtain an improved estimate of α_1 . Then (226) can be used to obtain the reactance matrix. Partial cross-sections may be obtained from the reactance matrix using well known formulas.

In the event $\det \mathbf{M}^{11}$ is very small, (257) is numerically ill-conditioned. Nesbet suggested when a similar problem occurs in the algebraic solution of the close-coupling equations¹⁴ that if $\det \mathbf{M}^{11}$ is smaller than $\det \mathbf{M}^{00}$ we should solve for the reciprocals of the reactance matrix elements instead of for the reactance matrix elements. Thus

$$\alpha_{ip}^0 = \delta_{ip} \quad (260)$$

Then the reactance matrix elements are given by¹⁴

$$R_{ip}^{-1} = \left(\frac{v_i}{v_p} \right)^{1/2} \alpha_{ip}^0 \quad (261)$$

and the variational principle is¹⁴

$$\delta \left[I_{pq} + \left(\frac{\hbar}{2a_0} \right) v_p \alpha_{pq}^0 \right] = 0 \quad (262)$$

which has been called the inverse Kohn or the Rubinow variational principle. Then

$$\alpha_0^1 = \alpha_0^0 + \left(\frac{2a_0}{\hbar}\right) V^{-1} I \quad (263)$$

The Rubinow variational method leads to

$$\alpha_0^0 = -(M^{00})^{-1} M^{01} \quad (264)$$

where the details of the derivation are similar to those before. The choice as to whether to use the Kohn or Rubinow variational principle is sometimes arbitrary. In the anomaly-free method¹⁴ the former is used if $\det M^{00}$ is smaller than $\det M^{11}$ and vice versa.

Note that if the minimum-norm method is used to determine α_0 and α_1 , neither (225) nor (260) holds. In that case we use

$$R = V^{1/2} \alpha_1 \alpha_0^{-1} V^{-1/2} \quad (265)$$

instead of (226) or (261).

The method presented in this section is not an alternate derivation of the Harris-Michels results. The reactance matrices and wave functions obtained from these equations are different from those obtained from the Harris-Michels equations. The main advantage of the present method is that the equations are derived using the usual scattering variational principle (the Kohn variational principle). Thus the procedure represents the most general application of the Kohn variational method. It should be useful because the results can be compared more directly to other results obtained by the Kohn variational method but using a more restricted trial function. A further value of the equations here is in tying together three different approaches: the applications of the Kohn variational method to the algebraic close-coupling equations by Nesbet and to correlation functions by Miller and others, and the use of the Harris and Michels trial function (which, as discussed in Section III.D, is the methodologically simplest version of the algebraic correlation method trial function).

D. Algebraic Correlation Method

We now consider application of the Kohn variational principle to the trial function

$$\psi^p = \sum_{i=1}^P \left[Y_{ip}^0(r_i) + \sum_{a=1}^{n_i} c_{ap}^i \eta_a^i(r_i) \right] f_i(x_i) + \sum_{m=1}^{n_q} c_{mp} W_m(r_i, x_i) \quad (266)$$

where the α_{0ip}^0 , α_{1ip}^0 , c_{ap}^i , and c_{mp} are coefficients to be determined. This may be considered to be an algebraic version of the correlation method discussed previously by Gailitis, Burke and Taylor, and Miller (see

Section III.B). The Harris and Michels-type trial function may be considered to be a special case of (266) in which only the free terms and the correlation terms are retained. Conversely, (266) may be considered to be a special case of the Harris and Michels-type trial function in which some of the correlation functions W_m are of the separable form $\eta_a^i f_i$. The treatments here of the trial functions (222) and (266) are numerically equivalent when the W_m 's in (222) are chosen in such a way as to make (222) and (266) identical. The new terms (of the form $c_{aa^i} \eta_a^i$) in (266), as opposed to (222), will be called "bound terms." The new problem posed by explicit use of (266) is the determination of their coefficients. This may be done using the procedure (the Kohn variational principle) used by Nesbet¹⁴ for the algebraic close-coupling problem. This leads to the same type of equations as in the previous section but with the following important changes:

$$J_{m\alpha} \rightarrow \sum_i \langle W_m | H - E | (Y_{i\alpha}^0 + \sum_a c_{aa^i} \eta_a^i) f_i \rangle \quad (267)$$

$$M_{ij}^{\alpha\beta} \rightarrow \langle A_{i\alpha}^0 f_i | U | A_{j\beta}^0 f_j \rangle \quad (268)$$

where

$$U = M - \sum_{\alpha r} \sum_{ab} M |\eta_a^{\alpha} f_a\rangle \langle \eta_a^{\alpha} f_a| M^{-1} |\eta_b^{\alpha} f_b\rangle \langle \eta_b^{\alpha} f_b| M$$

Finally the coefficients of the bound terms in the trial function are given by

$$c_{aa^i} = \sum_r (\alpha_{0ra}^0 c_{a0}^{ir} + \alpha_{ira}^0 c_{a1}^{ir}) \quad (269)$$

where the $c_{aa^i}^{ir}$ satisfy

$$\sum_s \sum_b \langle \eta_a^{\alpha} f_a | M |\eta_b^{\alpha} f_b\rangle c_{ba}^{\alpha s} = -\langle \eta_a^{\alpha} f_a | M | A_{aa}^0 f_a \rangle \quad \alpha = 0, 1 \quad (270)$$

where the trial values α_{ani}^0 should be used in (270).

The generalization of this treatment to include closed channels in the close-coupling part of the trial wave function [i.e., to replace the first part of (266) by (224)] can be accomplished in a straightforward way.

The reasons why one might wish to single out certain of the square-integrable basis functions for inclusion in the bound-term sum instead of the correlation-term sum are various. One of them is for explicit close-coupling type of interpretations of the scattering process in terms of contributions from various target eigenstates. Of course such interpretations can also be made using the Harris and Michels-type trial function, but in that case the interpretation is less direct because the W_m must first be projected on the f_i . A second reason is for ease in checking the computations (both for coding errors and for completeness of a basis set) using the algebraic variational method against numerical integration of the correlation method integrodifferential equations. It appears that such comparison (see, e.g., Ref. 17) of the algebraic methods with numerical

integration methods is very useful, at least until more experience is gained with the algebraic methods. In the form of (266), the wave functions can be compared most directly. Further, in this form one can compare other elements of related treatments (e.g., the potential matrix elements of the algebraic correlation method with their analogues in the algebraic close-coupling method) to discover how additional flexibility in the wave function affects the results in detail. A third use for the equations in this section is that they provide a link to make explicit the connection between the correlation method of Miller and others and the method of Harris and Michels. The relation between this section and the method of Harris and Michels is that the trial functions (but not the methods of determining the coefficients) are formally equivalent. The relation between this section and the correlation method is discussed in Section III.B.

E. Discussion of Above Methods

The schemes of Sections III.C and III.D combine the use of correlation terms in the trial wave function expansion with an algebraic variational approach to the calculation. The advantages of correlation terms have been discussed in the references to Section III.B and the advantages of algebraic variational methods have been discussed in Section I, but it is perhaps worthwhile to discuss these points further.

Correlation terms may be used to put special physical features of the compound system into the trial function. This often requires expressing these terms in a coordinate system different from the one in which the scattering boundary conditions achieve their most natural form. For example, for electron-atom scattering it may be desired to express the W_m in terms of interelectronic coordinates (r_{ij}), or for chemical reactions it may be desired to express the W_m in terms of transition-state normal coordinates. Another example, which has applications for all kinds of collisions, is to use the correlation terms to include so-called perturbed stationary states (also called polarized orbitals in electron scattering or molecular states in high-energy atom-atom scattering). Another example of their use is to include specific compound resonance states. Or we may think of the purpose of correlation terms as a way to effectively include virtual target continuum contributions even when the target does not really break up. In the Harris and Michels-type function the correlation terms not only carry out these special purposes but also perform the role of the target-eigenstate terms of the close-coupling approximation. In general we can think of these terms as providing a convenient method of making the expansion of the trial wave function effectively complete. The advantage of the algebraic approach is that it obviates the need to solve very large sets of coupled (integro) differential equations for the wave function. Even

with the latest techniques this can be very time-consuming. Alternatively we can think of the algebraic method as being a new and the very latest method of solving the coupled (integro) differential equations.

It should be clear that if the form (222) of the wave function spans the same space as the form (223) then the former will lead to the same algebraic problem. The advantages of (222) over (223) are (a) the important possibility of using a more general trial function as discussed in the preceding paragraph and (b) the minor advantage of reducing the number of subscripts on the coefficients.

We did not require the correlation terms to be orthogonal to the free functions. Although Harris and Michels explicitly made their correlation terms orthogonal to their free functions,¹⁵ this is not really necessary even for their method. This is proved in Appendix 1.

The variational principles used here allow us to variationally improve the reactance matrix elements (or their reciprocals) but they do not allow us to improve the rest of the trial wave function. Unlike the case where point-by-point variations are allowed, the algebraic method does not allow us to obtain any trial wave function whose asymptotic form corresponds to the variationally correct $R_{i,p}$. The advantage of variationally improved results is that errors in the $R_{i,p}$ are second order in the errors in the wave function. Thus the calculated scattering cross-sections are not as sensitive to the deficiencies of the basis set as when nonvariational techniques are used and are not as sensitive to these deficiencies as the trial wave function.

We should point out that for the combination of reasons discussed in the last three paragraphs the extension of the Harris, Michels, and Nesbet methods presented here is probably at this time one of the most economical and straightforward general ways to obtain the wave function for most scattering problems, including inelastic electron scattering and chemical reactions. If one desires to obtain directly the scattering probabilities (not the wave function), one of the methods dealing directly with the transition matrix^{107,133} may be preferable. For example, Baer and Kouri¹³³ have developed an algebraic technique for solving for "channel operators" and amplitude densities (from which the cross-sections and wave functions may then be calculated). It is being extended to include the use of correlation functions by using a variational principle.¹³⁴ Reinhardt has also presented a new method that requires neither expansion of the wave function in a basis nor numerical integration of coupled (integro) differential equations.¹³⁵ In Section III.F we consider other algebraic variation methods which involve expansion of the wave function in a basis set.

Next we consider a few illustrative calculations on elastic electron-hydrogen atom scattering using algebraic close-coupling methods. We consider the singlet electron-spin state. Then we need not explicitly include

TABLE V
Basis Set for Electron-Hydrogen Atom Scattering
Calculations of Figs. 5 to 11^a

a^b	ζ_a
1	0.005
2	0.01
3	0.02
4	0.05
5	0.15
6	0.4
7	0.7
8	1.1
9	1.5
10	3.0

^a The calculations were performed by the algebraic 1s-2s-2p close-coupling method (including exchange) as described by Seiler et al.¹⁷ as modified in Ref. 146. Two free functions $[(1 - e^{-r})^3 j_1(kr)$ and $(1 - e^{-r})^3 \xi_1(kr)]$ were used, and the short-range parts of the four channel functions were each expanded in terms of 10 Slater-type functions of the form $r^l e^{-\zeta_a r}$, with $a = 1, 2, \dots, 10$. Note that distances are in bohrs.

^b See (224) where $P = 4$, $n_i = 10$, and $Q = 4$.

spin in the wave function, but the wave function must be symmetric under interchange of the two electrons' spatial coordinates. These calculations use as trial function the symmetrizer times the function of (222) with $P = 1$ and $M = 40$. We consider the case where the total angular momentum is $L = 1$. The basis set is explained in Table V. The bound-bound Hamiltonian matrix

$$H_{\alpha\alpha}^{\eta\eta} = \langle W_\alpha | H | W_\alpha \rangle \quad (271)$$

has 40 eigenvalues E_μ . The lowest twelve are listed in Table VI. The analysis of Section II.H, which is based on Nesbet's work,¹³ may be extended to the multichannel scattering problem, and we would expect the Kohn and Rubinow methods to show spurious structure near but not exactly at the energies where E equals one of the E_μ .^{136,62}

Fig. 6 illustrates the poles in the $M_{11}^{\alpha\beta}$ which occur near the fifth, sixth, and seventh eigenvalues of $H^{\eta\eta}$. Fig. 7a shows t_R^0 and t_R^R for the energy region near the fifth and sixth eigenvalues of $H^{\eta\eta}$. t_R^0 shows two pseudo-antiresonances and t_R^R shows two pseudoresonances. Except in these two regions t_R^0 is too close to t_R^R to be distinguished on the plot. Further, at

TABLE VI

Lowest Twelve Eigenvalues E_μ of H^{77} for $L = 1, S = 0$ for the Basis Set of Table V

μ	E_μ (Ry)	k_μ^2 (a_0^{-2})
1	-0.9999842	0.0000158
2	-0.9999081	0.0000919
3	-0.9995379	0.0004621
4	-0.9973415	0.0026585
5	-0.9838141	0.0161859
6	-0.9321195	0.0678805
7	-0.7936308	0.2063692
8	-0.4424070	0.5575930
9	-0.2517707	0.7482293
10	-0.2500602	0.7499398
11	-0.2499964	0.7500036
12	-0.2499806	0.7500194

the fifth eigenvalue of H^{77} the pseudoantiresonance of t_R^0 is so narrow it is hidden behind t_R^R on the plot.

Although there has been much discussion of how to tell spurious singularities from real resonances, one very important practical method has not been mentioned in the literature. At a real resonance, both the uncorrected and the corrected phase shift increase by π . If, as in the present example, either the corrected or the uncorrected phase shift decreases by π , then the resonance is not real.

Fig. 7b shows t_K^0 and t_K^K in the same energy region. Figs. 7a and 7b have been drawn so they partially overlap; thus it is clearly seen that at the positions of the two pseudoresonances of Fig. 7a (where Fig. 5 shows M_{11}^{00} and M_{11}^{01} have correlated zeroes), t_K^0 and t_K^K are smooth. Instead t_K^0 and t_K^K show spurious structure where M_{11}^{10} and M_{11}^{11} show correlated zeroes. Actually M_{11}^{10} shows four zeroes in this energy region. The third of these (at $k^2 = 0.088a_0^{-2}$) does not cause any extra spurious structure but is associated with the phase shift passing smoothly through zero. Similarly the third zero of M_{11}^{00} (at $k^2 = 0.112a_0^{-2}$) does not cause a third region of spurious structure in t_R^0 or t_R^R but is associated with the phase shift passing smoothly through zero. This again emphasizes the need to consider correlated zeroes of the M_{11}^{ab} . It is also interesting to notice that the reason the spurious structure associated with t_K^0 and t_K^K occurs at an energy so much different from the energy of the seventh eigenvalue of H^{77} is that the "background" M_{11}^{10} and M_{11}^{11} are near zero. Nevertheless, Fig. 5 shows the spurious structure is unequivocally attributable to the influence of the seventh poles of M_{11}^{10} and M_{11}^{11} .

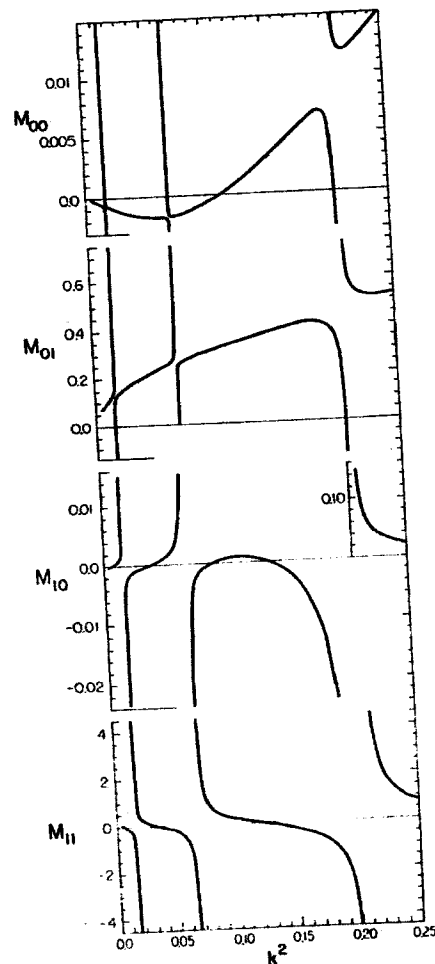


Fig. 6. The quantities M_{11}^{00} , M_{11}^{01} , M_{11}^{10} , and M_{11}^{10} (in Rydbergs) as functions of k^2 (in atomic units) for elastic scattering of an electron off the ground state hydrogen atom with $L = 1$ and $S = 0$. The calculations were made with the basis set of Table V and are shown in the vicinity of the fifth, sixth, and seventh energies where M^{nn} has a zero eigenvalue. In the figures the M_{11}^{ab} are labeled M_{ab} as in Ref. 13.

Fig. 7c shows the Hulthén method results in this energy region. As expected the Hulthén method predicts complex phase shifts in two energy intervals. Near the sixth eigenvalue of H^{nn} , the figure also shows a sudden change in slope of the phase shift predicted by this method just to either side of the interval where complex values are obtained (nothing is plotted for this interval). This region is shown with an expanded abscissa in Fig. 8.

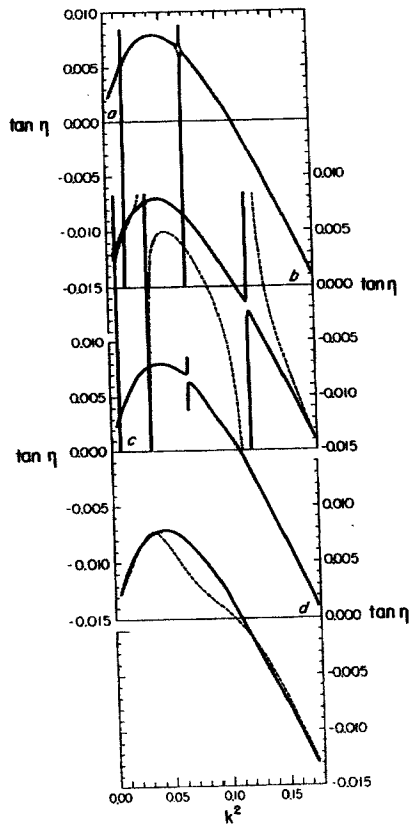


Fig. 7. The tangent of the phase shift for elastic scattering of an electron off the hydrogen-atom with $L = 1$ and $S = 0$ as a function of k^2 (in atomic units). The calculations were made with the basis set of Table V and are shown in the vicinity of the fifth, sixth, and seventh energies for which M^{nn} has a zero eigenvalue. (a) The solid line is the result t_R^R of the corrected Rubinow method and the dashed line is the result t_R^0 of the uncorrected Rubinow method. The results using the uncorrected and corrected Rubinow method are practically the same on this scale, except in the regions of the two pseudoresonances where the two results tend to infinity in opposite directions; that is, the corrected Rubinow result shows pseudoresonances and the uncorrected Rubinow result shows pseudoantiresonances. (b) The solid line is the corrected Kohn result t_K^K and the dashed line is the uncorrected Kohn result t_K^0 . The corrected Kohn result shows three pseudoresonances and the uncorrected Kohn result shows two pseudoresonances followed by a pseudoantiresonance. (c) The solid line is the result t_H of the Hulthén method. The only spurious structure that appears here is in the region of the sixth zero eigenvalue. The spurious structure in the region of the fifth zero eigenvalue is too small to be seen on this scale, and the structure due to the seventh zero eigenvalue occurs at higher k^2 . (d) The solid line represents the results t_{MN}^K and t_{MN}^{MN} of the minimum-norm method corrected with either the Kohn or the minimum-norm variational expression (the two results are indistinguishable). The dashed line represents the result t_{MN}^0 of the uncorrected minimum-norm method.

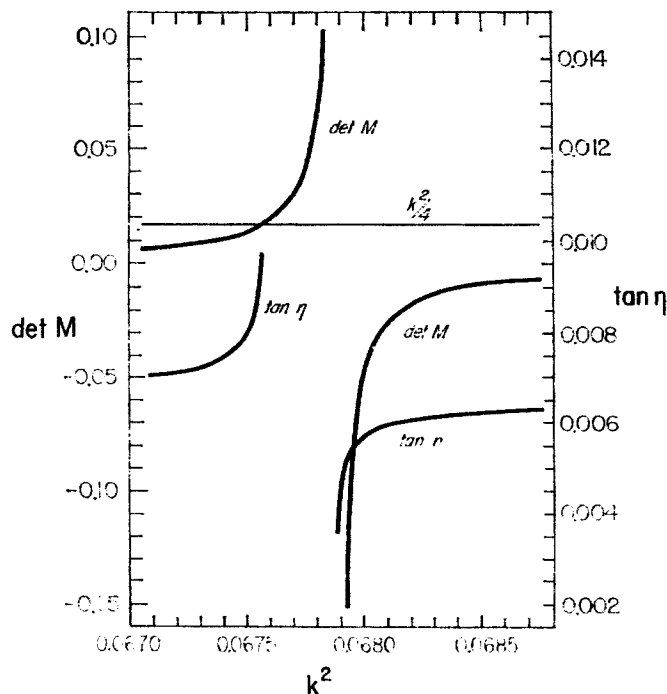


Fig. 8. The three solid curves represent the left- and right-hand sides of inequality (77) in Ry^2 , and the tangent of phase shift obtained by the Hulthén method as functions of k^2 (in atomic units) for the electron-hydrogen scattering problem of Fig. 7 in the vicinity of the sixth energy where $M^{(n)}$ has a zero eigenvalue. The Hulthén result for the tangent of the phase shift becomes complex at the energy where the curves whose numerical values in Rydberg atomic units are $DET M$ and $k^2/4$ cross and remain complex until sixth energy where $M^{(n)}$ has a zero eigenvalue.

We see the pole in $DET M_{11}$ and the interval where complex values are obtained. This figure illustrates the discussion of (77). Hopefully, the figure will make the previous discussions^{13,16} more clear.

Fig. 7d shows the minimum norm results in the vicinity of the fifth and sixth eigenvalues of $H^{(n)}$. The zero-order minimum norm result shows no spurious structure but is very inaccurate. In a certain sense, this can be blamed on (110). For example, at the sixth eigenvalue of $H^{(n)}$, t_R^0 , t_K^0 , and t_{MN}^0 are all equal. But the slopes of phase shifts are very different. The requirement of equality of the phase shifts at the eigenvalue of $H^{(n)}$ does not give much clue to the value of t_R^0 elsewhere because it has a pseudo-antiresonance near there and so it assumes all values from $-\infty$ to $+\infty$ in this region. But t_{MN}^0 is smooth and so the fact that it is bad at the eigenvalue of $H^{(n)}$ means it is also bad far from the eigenvalue. Thus t_{MN}^0 is less

accurate than t_R^0 in general. In general t_{MN}^0 is not very accurate but t_{MN}^{MN} is very accurate. Further we have not ever found any spurious structure in t_{MN}^0 or t_{MN}^{MN} . Evidently the minimum-norm method with the variational correction⁵⁰ we have called the minimum-norm variational expression has overcome the problem of correlated zeroes in the numerator and denominator of the formula for the tangent of the phase shift. Unfortunately t_{MN}^{MN} is the only method (of those being considered in this section) for which an extension applicable to inelastic scattering has never been given. The minimum-norm zero-order method corrected with the Kohn or Rubinow variational expression as recommended in Refs. 15 and 16 sometimes shows spurious structure (see Section II.H).

Figs. 9 and 10 show M_{11}^{ab} in the energy region near the ninth eigenvalue of H^{00} . Figs. 11 and 12 show the calculated phase shifts in this energy region. This eigenvalue corresponds to a real resonance, the lowest 1P

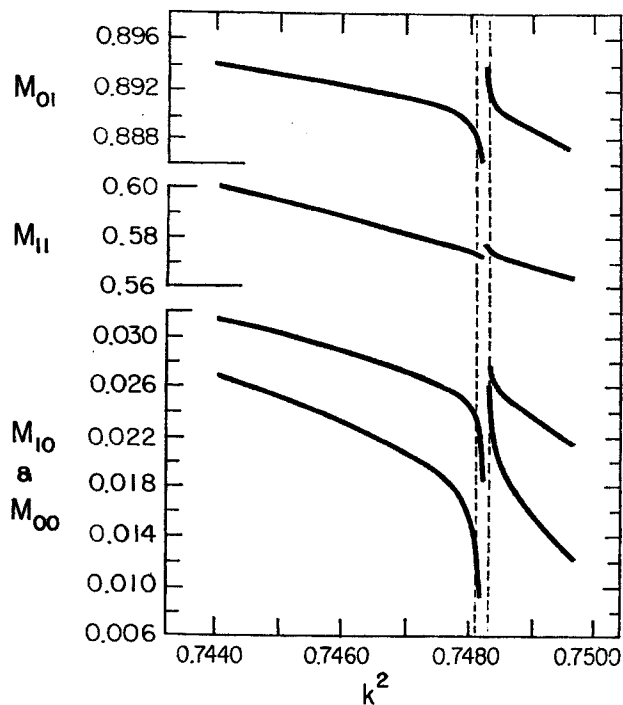


Fig. 9. The quantities M_{11}^{00} , M_{11}^{01} , M_{11}^{10} , and M_{11}^{11} (in Ry) as functions of k^2 (in atomic units) for elastic scattering of an electron off the ground state hydrogen atom with $L = 1$ and $S = 0$. The calculations were made with the basis set of Table V and are shown in the vicinity of the ninth energy at which M^{00} has a zero, that is, in the vicinity of the first 1P resonance.

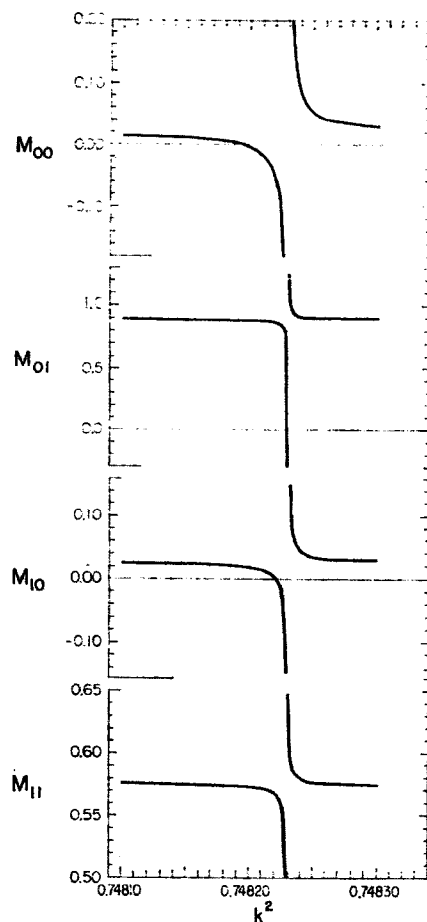


Fig. 10. The quantities M_{11}^{00} , M_{11}^{01} , M_{11}^{10} , and M_{11}^{11} (in Ry) as functions of k^2 (in atomic units) for the energy region bounded by the dashed lines in Fig. 9.

resonance.^{17,93,118} (Note: this should not be confused with the second-lowest ¹S resonance,^{17,93,118,129,137} which is at just about the same energy.) In this case M_{11}^{11} and M_{11}^{01} each shows its zero very close to the eigenvalue of H^m . The zeroes of M_{11}^{00} and M_{11}^{10} are farther from the eigenvalue of H^m . These features are consequences of the background phase shift being near zero and the resonance being very narrow. Notice that all seven calculations shown in Fig. 12 show the resonance correctly; none of the methods shows antiresonance behavior when the resonance is real. In

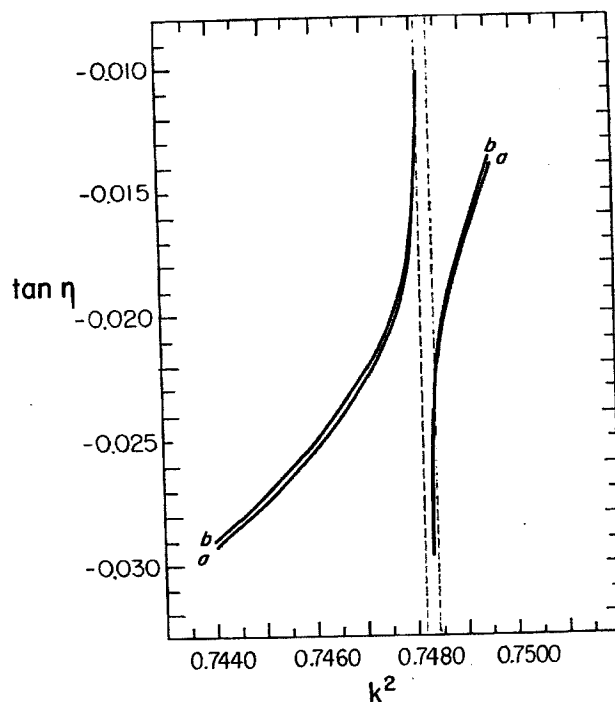


Fig. 11. The tangent of the phase shift for the electron-hydrogen atom problem and energy region of Figs. 9 and 10 as a function of k^2 (in atomic units). The curve marked *a* is the corrected Rubinow result, and the curve marked *b* is the corrected Kohn result.

addition, notice that the Kohn method is accurate in this region even though M_{11}^{11} has a zero in this region.¹³⁸

The same type of analysis of spurious singularities and real resonances may be given for cases where more than one channel is open. Although the general principles are the same the details are more complicated.

Other valuable analyses of the spurious singularities in the Kohn and Rubinow methods for the case where only one channel is open have been given by Brownstein and McKinley,⁴³ Kolker,⁶¹ Shimamura,⁶² and Payne.¹³⁹ In particular Shimamura's analysis leads to $(M + 1) \times (M + 1)$ matrices N^S and N^C defined similarly to N [see (239)] but with $W_{M+1}(r_1, x_1)$ equal to $A_{10}(r_1)$ or $A_{11}(r_1)$, respectively. The spurious singularities of the Kohn method are then identified with energies where $\det N^S$ is zero, and the spurious singularities of the Rubinow method are identified with energies where $\det N^C$ is zero. These criteria are essentially the same as

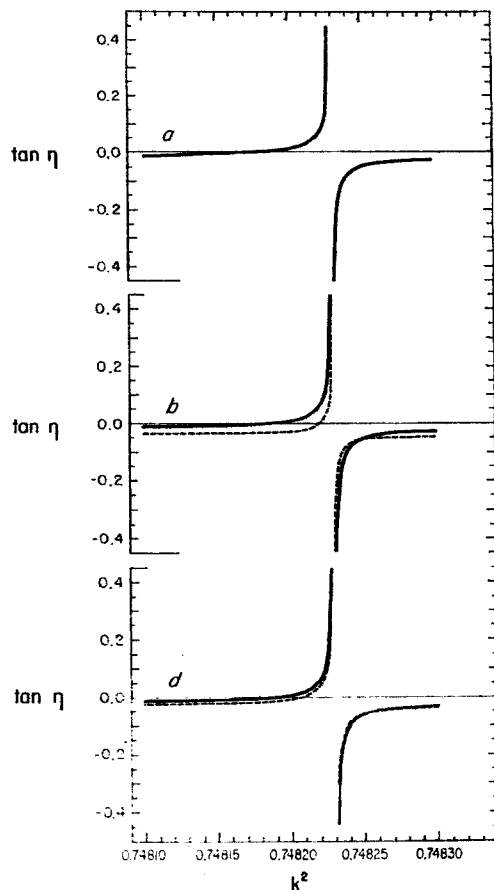


Fig. 12. The tangent of the phase shift as a function of k^2 (in atomic units) for the energy region bounded by the dashed lines in Fig. 11. (a) The results of the uncorrected Rubinow, the corrected Rubinow, and the Hulthén methods are all represented by the one curve. (b) The solid curve is the result of the corrected Kohn method and the dashed curve represents the result of the uncorrected Kohn method. (c) The solid curve represents the results for both the minimum-norm method corrected with either the Kohn correction or the minimum-norm correction. The dashed curve represents the result of the uncorrected minimum-norm method.

Nesbet's but may sometimes be more convenient. These $(M + 1) \times (M + 1)$ matrices also occur in Kolker's analysis⁶¹ of how many basis functions must be added before convergence becomes monotonic in the Kohn and Harris methods for potential scattering.

It is sometimes useful^{119,130,131,140} to separate the problems associated with nonmonotonic convergence as more basis functions are added in the

open channels [i.e., as the n_i in (266) are increased] from the problems of convergence as the closed-channel portion of the wave function is made complete [i.e., as n_Q in (266) is increased]. The former problems are analogous to the convergence problems of potential scattering, and the latter errors are those for which the minimum principles of Spruch and others are applicable when the open-channel part of the wave function is treated exactly.

There have been a number of applications of the algebraic variational methods of the type discussed so far in this section to model problems^{14,15,48,84,141} and to electron-atom^{8,10,11,17-19,37,38,40,42,62,71,83,124-126,129-131,142-146} and positron-atom^{11,17,18,37,125,127,144,147,148} scattering but only two applications to other processes; that is, Massey and Ridley^{37a} applied the Kohn and Hulthén variational methods to electron-hydrogen molecule scattering and Mortensen and Gucwa applied the Kohn variational method to collinear chemical reactions.¹⁴⁹ In most of these calculations only the corrected results are presented but in a few cases^{16,18,126,127,144,139,146} zero-order results are presented also. We next summarize the applications to electron-atom and positron-atom scattering.

For electron-atom scattering the close-coupling method with $P = 1$ is the continuum Hartree method, and the algebraic close-coupling method with $P = 1$ is the continuum matrix Hartree method. Antisymmetrizing the trial wave function leads to the continuum matrix Hartree-Fock method. If we consider simultaneous variation of the bound orbitals and the continuum orbital in a one-configuration wave function we find the variationally correct bound orbitals are the ones that would be obtained in the absence of the continuum orbital; that is, the problem separates into two independent problems which must be solved in order— one for the bound orbitals in the many-electron wave function $f_i(x_i)$ in the absence of the continuum orbital and one for the continuum orbital $X_{i,p}^0(r_i)$ in the presence of the bound orbitals. One way to obtain this result is to put the system in a large box and normalize all the orbitals by integrating over all space. Then the continuum orbital has vanishingly small amplitude in the region where the bound orbitals are nonzero. One way to introduce correlation of the bound and free orbitals is to introduce extra open-channel configurations or extra square-integrable configurations. But the most general function possible is always a special case of (222). Equation (222) includes as special cases the continuum analogues of both the configuration interaction method and the multiconfiguration self-consistent field methods. In summary, in the first part of the calculation the forms of the terms $f_i(x_i)$ in the wave function at large r_i are determined independently in a bound-state calculation. In the second part of the calculation, the coefficients of terms which do not vanish at large

r_i and the form of the wave function at small r_i are determined. In algebraic variational calculations both these parts of the whole scattering problem consist of determining coefficients of preselected functions.

In classifying the calculations we consider all trial functions as special cases of (222) and we distinguish the methods by the procedure used to find the matrices α_0^0 and α_1^0 . Calculations in the static approximation are reviewed in Section II. Elastic scattering calculations for energies below the inelastic threshold using other approximations are summarized in Table VII. For elastic scattering a few calculations have been carried out by methods discussed in Section III.F; these are not included in the table. All the inelastic electron-atom and positron-atom scattering calculations using algebraic methods that have ever been reported are summarized in Table VIII. In addition Matese and Oberoi used their calculated wave functions to study photodetachment.¹⁴³

There have also been a number of articles¹⁵⁰ concerned solely with integrals that occur in electron-atom scattering using algebraic variational methods. The methods used for these integrals may also be used for partial-wave Born and Born-Oppenheimer approximation^{40, 151, 152, 153} calculations.

F. Other Methods

One disadvantage of the close-coupling method, the algebraic close-coupling method, the other methods discussed above, and many other methods for solving scattering problems is that the same variational function is used at small r_i (the interaction region, where a large basis set is usually necessary) as is used at large r_i (in the near-asymptotic regions of the various channels, where a small close-coupling basis with no or few closed channels should be sufficient). A few procedures have been devised for decreasing the size of the close-coupling basis set during a calculation as one integrates out toward large r_i .^{102, 103} In addition, other methods similar in spirit to Wigner's derivative matrix (R -matrix) method have been used to divide the problem into an interaction region and an external region. Such techniques will probably become very important as more practical calculations are attempted. These techniques can be refined further if necessary. For example, we can apply the Kohn-Crawford variational method⁷⁰ to the close-coupling equations but use a successively smaller expansion basis in each of several different regions. If each successively smaller basis set were a subset of the previous one, that is, if the basis sets were nested, such a calculation would not present great difficulties in starting a calculation in region 2 (from $r_i = a$ to $r_i = a'$) using the result of the region 1's calculation at $r_i = a$ as boundary conditions to be satisfied by the trial function in region 2. As the number of

TABLE VII
Algebraic Variational Electron-Atom and Positron-Atom Scattering Calculations (Excluding Static Approximation) When There is Only One Open Channel Using Methods Discussed in Sections III.B to III.E

Reference(s)	Projectile(s)	Target(s)	M	Method(s) ^a	Where done
8	e^-	H	2-4	EI	Williams Bay
37	e^-	H	1	K, H	London
37b	e^+	H	1-2	K, H	London
37c	e^+	H	1-2	K, H	London
37d	e^+	H	2-3	K	New York
38	e^-	H	0-2 ^b	H	Oslo
124	e^-	He	1	H	Belfast
40	e^-	H	1	K, H	Glasgow, Belfast, and London
10, 11	e^-, e^+	H	3-50	K	Berkeley
125	e^-, e^+	H	1-70	K	Berkeley & Monterey
42	e^-	H	1-2	K, R, H, M, John	Cardiff
126	e^-	H	>7	Harris	East Hartford
126, 16	e^-	He	<138	Harris	East Hartford
16	e^-	H	3-34	H, K, R, MN-K or MN-R	Salt Lake City and East Hartford
139	e^-	H	7-34	K ^d	Iowa City
142	e^-	H	45	AF	Baton Rouge
17	e^-, e^+	H	45-48	AF	Baton Rouge
127	e^+	H, He	4-85	Harris	Greenbelt
143	e^-	H	35-50	AF	Baton Rouge
129	e^-	H	17	K, R, or AF	San Jose
130, 131	e^-	H	Not given	K	Raleigh and LaJolla
18	e^-, e^+	H	50-56	K, Harris	Tokyo
144	e^-, e^+	He ⁺ , Li ²⁺ , Be ³⁺ , B ⁴⁺	50-56	Harris	Tokyo
19	e^-	H	2-6	K, R, AF, MN-K ^d	Minneapolis
147	e^+	H	Not given ^c	K, R	Baton Rouge
145	e^-	He	20-72	AF	San Jose
71	e^-, e^+	H, He ⁺	8-24	AF	San Jose
148	e^+	H	4-23	K	London
62	e^-	H	54-70	K	Tokyo

^a EI, Euler integral; K, Kohn; H, Hulthén; AF, anomaly-free; R, Rubinow; MN-K, minimum norm corrected with the Kohn variational expression; MN-R, minimum-norm corrected with the Rubinow variational expression.

^b Staver also added a polarization potential to some of his calculations.

^c In two cases M is given (30 and 100). Note: M is defined in equation (222).

^d See also Section III.F.

TABLE VIII

Algebraic Variational Electron-Atom and Positron-Atom Scattering Calculations for Cases With More Than One Open Channel Using Methods Discussed in Sections III.B to III.E

Ref- erence(s)	Pro- jectile(s)	Target(s)	N_O ^a	M	Method(s) ^b	Where done
83	e^-	H	2	1	c	London and Belfast
17	e^-, e^+	H	2-3	30-45	AF	Baton Rouge
146	e^-	H	4	28-60	K, R, AF, MN-K	Minneapolis
129	e^-	H	3	16	K, R, or AF	San Jose
147	e^+	H	2	30-100	AF	Baton Rouge
148	e^+	H	2	35-84	H, K, R, AF	Jerusalem

^a N_O is number of open channels included in trial function.

^b AF, anomaly-free; K, Kohn; R, Rubinow; MN-K, minimum-norm corrected with the Kohn variational expression; H, Hulthén.

^c Method of Ref. 82.

regions becomes larger it is hard to distinguish such an algebraic variational calculation from a numerical integration. For example, the technique just described resembles in some respects some of the numerical integration techniques now popular for scattering problems which involve obtaining the solution approximately in terms of analytic functions in successive intervals and matching the solutions in different intervals at the boundaries.^{154,155}

An even more striking illustration of the difficulty of distinguishing basis set expansion techniques from other methods is the fact that the finite difference methods using central differences can be reformulated as variational calculations using spline-like basis functions.¹⁵⁶ Thus the finite difference methods using central differences¹⁵⁷⁻¹⁵⁹ may be classified as algebraic variational methods.

Having pointed out the difficulty of clearly sorting types, we now discuss a few examples of approaches using basis sets for wave functions which have recently been of interest in chemical physics scattering problems.

The derivative matrix technique and other techniques involving artificial channel boundaries have been extended to the treatment of multichannel scattering problems in many ways and have been much analyzed in nuclear physics.^{68-70,160} Although much of the analysis has been formal¹⁶¹ there have been some computational applications. Recently some specific procedures for incorporating derivative matrix techniques into chemical physics scattering calculations have been suggested. There have been applications to electron-atom scattering, to a model problem, and to

collinear chemical reactions.¹⁶²⁻¹⁶⁶ Except for considerations of resonance energies and widths,¹⁶⁷ the other artificial channel radii techniques have received less attention in chemical physics so far. However, Crawford has extended the Kohn-Crawford method to the treatment of collinear chemical reactions,⁷¹ and Oberoi and Nesbet have extended the Kohn method with numerical asymptotic functions to electron-atom scattering in the exchange approximation.⁷² These methods have the advantages that calculations in the difficult to handle internal region are performed using techniques similar to those used in bound-state calculations, that the trial wave function is continuous and has a continuous first derivative, and that the scattering results are variationally corrected through first order and stationary.

Schlessinger¹⁶⁸ and McDonald and Nuttall and their co-workers¹⁶⁹⁻¹⁷¹ have extended the method of Schlessinger to multichannel problems. The latter workers use a generalization of the original method in that the wave functions are calculated for complex energies instead of negative energies. These calculations can be carried out algebraically. The calculation of free-free integrals is avoided but a troublesome extrapolation procedure must be introduced. McDonald and Nuttall⁷⁵ have extended the rotation method (i.e., the method of complex coordinates) to treat neutron-deuteron scattering. They feel that this method compares favorably to the complex-energy method¹⁶⁹⁻¹⁷¹ and the Kohn variational method.

Weare and Thiele¹⁷² have performed algebraic variational calculations on collinear atom-diatom molecule scattering using a method which resembles the Schwinger variational method.

Payne^{139,173} developed an algebraic variational method based on compact operators which reduces the scattering problem to a discrete eigenvalue problem. The method is applicable to single-channel and multichannel problems and Payne applied it to elastic electron-hydrogen atom scattering.

Garrett¹⁷⁴ presented two methods for multichannel elastic scattering problems based on the trial function (220) with $P = 1$. In both methods, a trial potential $V_t(r_i)$ is chosen and the equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr_i^2} + \frac{l(l+1)\hbar^2}{2mr_i^2} + V_t(r_i) - E \right) X_{11}^0(r_i) = 0$$

is solved numerically to obtain $X_{11}^0(r_i)$ and a trial phase shift η_l^t . In method 1, (229) is used to determine the coefficients $c_{m,p}$. Then one checks whether (230) is satisfied. If not, one varies V_t , obtains a new $X_{11}^0(r_i)$, and checks (230) again. One continues this trial-and-error procedure until (230) is satisfied. Garrett suggested that one also optimize nonlinear parameters in $W_m(r_i, x_i)$ by choosing the values that minimize $|I_{pq}|$. If one chooses the nonlinear parameters so that $I_{pq} = 0$, and if one channel is

open, the bounding principle¹⁶⁹ may be applied. In method 2, one does not use (230) but varies V_i until $I_{pa} = 0$. Garrett applied his method to electron and positron scattering by hydrogen atoms.

Knudson and Kirtman extended their variation-perturbation theory formalism, which uses the Hulthén method for the first-order wave function, to multichannel scattering.¹⁷⁵

Schwartz⁷⁹ and Rabitz and Conn¹⁷⁶ have considered variational expressions which use trial T matrices

$$T = -2i(1 - iR)^{-1}R$$

instead of trial wave functions. Schwartz's method uses the Schwinger variational expression (see Section II.M) and the method of Rabitz and Conn uses a variational expression due to Newton.¹⁷⁷

IV. ADDENDUM

Shortly after this article was submitted for publication, some additional related work became available; it is summarized briefly here, classified by the section to which it is relevant.

Section II.F: Wladawsky¹⁷⁸ proposed a new method—the variational least-squares method—which is very similar to the minimum-norm method.

Section II.H: Kolker¹⁷⁹ provided another discussion of the theorem^{43,61} (for central potential scattering) that after enough terms are added to the Kohn trial function the Kohn method provides a lower bound on the tangent of the phase shift.

Section II.J: Read and Soto-Montiel¹⁸⁰ applied the minimum variance method⁶⁵ to single-channel scattering problems.

Section II.L: Hazi¹⁸¹ presented a nonvariational generalization of the original Harris method to the problem of calculating the reactance matrix from square-integrable approximations to the scattering wave function for inelastic scattering. His method involves using an assumed functional form for the R -matrix elements and an iterative procedure. Heller and Yamani¹⁸² presented a variational method involving square-integrable trial functions which appears to be an improvement over the derivative matrix method.

Section III.E: Further variational calculations for positron-atom¹⁸³ and electron-atom¹⁸⁴ scattering and partial-wave-Born approximation calculations for positron-atom scattering¹⁸⁵ have been reported.

Section III.F: A discussion of some advantages of the derivative matrix method has been given.¹⁸⁶ Koppel and Lin¹⁸⁷ applied the Schwinger variational method to nonalgebraic trial functions obtained by non-variational methods for collinear atom-diatom collisions. Hazi¹⁸¹ applied his new method to a model multichannel scattering problem.

APPENDIX 1. ORTHOGONALITY IN THE HARRIS-MICHELS METHOD

Using the notation of Harris and Michels,¹⁶ we label the free functions ϕ_i and the correlation terms η_n .

We define orthogonalized free functions $\tilde{\phi}_i$ as

$$\tilde{\phi}_i = \phi_i - \sum_m S_{mi}^{\eta\phi} \eta_m \quad (\text{A1})$$

where

$$S_{im}^{\phi\eta} = \langle \phi_i | \eta_m \rangle \quad (\text{A2})$$

Then

$$M_{ij}^{\tilde{\phi}\tilde{\phi}} = \langle \tilde{\phi}_i | H - E | \tilde{\phi}_j \rangle \quad (\text{A3})$$

$$M_{in}^{\tilde{\phi}\eta} = \langle \tilde{\phi}_i | H - E | \eta_n \rangle \quad (\text{A4})$$

etc. Then

$$\mathbf{M}^{\tilde{\phi}\tilde{\phi}} = \mathbf{M}^{\phi\phi} - \mathbf{C} \quad (\text{A5})$$

where

$$\mathbf{C} = \mathbf{S}^{\phi\eta} \mathbf{M}^{\eta\phi} + \mathbf{M}^{\phi\eta} \mathbf{S}^{\eta\phi} - \mathbf{S}^{\phi\eta} \mathbf{M}^{\eta\eta} \mathbf{S}^{\eta\phi} \quad (\text{A6})$$

and

$$\mathbf{M}^{\tilde{\phi}\eta} (\mathbf{M}^{\eta\eta})^{-1} \mathbf{M}^{\eta\tilde{\phi}} = \mathbf{M}^{\phi\eta} (\mathbf{M}^{\eta\eta})^{-1} \mathbf{M}^{\eta\phi} - \mathbf{C} \quad (\text{A7})$$

Thus

$$\mathbf{M}^{\phi\phi} - \mathbf{M}^{\phi\eta} (\mathbf{M}^{\eta\eta})^{-1} \mathbf{M}^{\eta\phi} = \mathbf{M}^{\tilde{\phi}\tilde{\phi}} - \mathbf{M}^{\tilde{\phi}\eta} (\mathbf{M}^{\eta\eta})^{-1} \mathbf{M}^{\eta\tilde{\phi}} \quad (\text{A8})$$

But the Harris-Michels results are calculated from the right-hand side of (A8). Thus the results would be unchanged if we used the nonorthogonalized functions ϕ_i instead of the orthogonalized function $\tilde{\phi}_i$.

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26. A *variational principle* is an equation (derived, e.g., by the calculus of variations) that tells us that a certain quantity is stationary with respect to the allowed variations in the trial wave function. A variational principle can be used to write a *variationally correct expression* for a scattering quantity in terms of a trial wave function. The quantity computed from the variationally correct expression depends quadratically (not linearly) on the errors in the trial function. For example, a variational principle for a reactance matrix element allows us to calculate the first-order correction (first-order extrapolation toward the exact value) for an approximate reactance matrix element in a trial function. This correction is called a *variational improvement* in the matrix element. The corrected value is sometimes called the stationary value. A *variational functional* is a functional that appears in a variational principle. A *variational method* is a method that uses a variational principle to choose the parameters in a trial wave function. A variational method should involve as the final step the use of the variational principle and the trial function to calculate stationary values for the quantities of interest. However, the variational principle may also be applied to calculate first-order corrections to scattering quantities from trial functions which were not obtained by variational methods.
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spurious resonant behavior in the cross sections at eigenvalues of H^{η} . Although the distinction between the pseudoresonance positions and the eigenvalues apparently has no bearing on the results presented or the conclusions drawn in that paper, it is often important to distinguish these. Following Ref. 13, the text discusses how the Kohn and Rubinow methods introduce spurious resonant or pseudoresonant behavior in the cross-sections at paired zeroes of $\det M^{00}$ and $\det M^{01}$ and at paired zeroes of $\det M^{11}$ and $\det M^{10}$. These paired zeroes tend to occur near eigenvalues of H^{η} since all four $\det M^{\eta}$ have odd-ordered poles at such eigenvalues and since the $\det M^{\eta}$ generally have the shapes as functions of energy of the M_{11}^{η} shown in Figs. 6, 9, and 10. In this article we do not identify the resonance or antiresonance positions as the places where $\tan \eta$ or $\cot \eta$ is ∞ , but rather as the midpoint of the region where η is changing rapidly by π . (For problems with $P > 1$ one identifies the resonance or antiresonance as the midpoint of the region where the sum of the eigenphases is changing rapidly by π .) This is another important point that has caused confusion. For example, the discussion and formulas for positions and widths for pseudoresonances on p. 165 of Ref. 16 often yield the wrong position and too narrow a width. The error in position occurs because the discussion identifies the resonance with the place where $\tan \eta = \infty$. The width of the resonance was incorrectly assumed to be the width of the region where $\cot \eta \simeq 0$ rather than the width of the region where the phase shift increases rapidly by π . The width of the latter region depends on how close the zeroes of the numerator and denominator of the formula for $\tan \eta$ are, not merely on the width of the region over which the denominator is about zero.

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