PHYSICAL REVIEW VOLUME 175, NUMBER 1 5 NOVEMBER 1968

Analysis of the Harris Variational Method in Scattering Theory

R. K. Nesbet
IBM *Research Laboratory, San Jose, California* 95114
(Received 21 March 1968)

The variational method recently proposed by Harris for calculation of scattering phase shifts is analyzed in the context of the standard methods of Kohn and Hulthén. The Hulthén method is shown to give a result identical to the Harris method at the energy eigenvalues characteristic of the latter. The Kohn method and its analog for the cotangent of the phase shift, the second Hulthén or Rubinow method, lead to somewhat different limiting values of the phase shift at a Harris eigenvalue. The Harris method is an application to nonresonant situations of a formalism appropriate to scattering resonances. A new method is proposed to deal with stationary states, true resonances, and nonresonant scattering within a common formalism, which defines effective width and shift functions for all values of the energy in terms of a Breit-Wigner formula. The proposed resonance formalism is expressed in forms equivalent to the Rubinow method and to the Hulthén method. A method of smoothing out irregular behavior of computed Hulthén phase shifts, due to branch points at Harris eigenvalues, is proposed. The Kohn and Rubinow methods are shown to give smooth results near Harris eigenvalues. Spurious fluctuations encountered in computations by the Kohn method are shown to be due to poles not present in the Hulthén method. Similar poles occur in the Rubinow method, but at different energy values. A criterion is suggested for avoiding the irregular behavior due to these poles by making an appropriate choice of either the Kohn or the Rubinow formula at a given energy. The formal discussion is illustrated by some computed results for S-wave scattering by an attractive exponential potential.

I. INTRODUCTION

A new variational method for calculation of scattering phase shifts has recently been proposed by Harris[1] and applied to low-energy electron-hydrogen atom scattering by Michels and Harris.[2] In this method, applied to potential scattering, a variational function is constructed in the form

$$\phi_\mu = \sum_{i=1}^{n} \eta_i c_i^{\mu}, \tag{1}$$

where the basis functions η_i are quadratically integrable, and the coefficients c_i^{μ} satisfy the eigenvalue equation

$$\sum_j (\eta_i|H|\eta_j) c_j^{\mu} = E_\mu c_i^{\mu}, \quad i=1,\ldots,n. \tag{2}$$

The tangent of the phase shift, t, for a partial wave expansion, is determined by the condition

$$(\phi_\mu|H-E_\mu|S+tC)=0, \tag{3}$$

where S and C are, respectively, sine-like and cosine-like functions that are asymptotic eigenfunctions of H with energy, in atomic units,

$$E_\mu = \tfrac{1}{2}k_\mu^{2}. \tag{4}$$

For S waves, the Schrödinger equation is equivalent to a one-dimensional equation with

$$H = -\tfrac{1}{2}(d^2/dr^2) + V(r). \tag{5}$$

The unnormalizable functions S and C are asymptotically

$$S \sim \sin kr, \tag{6}$$

$$C \sim \cos kr. \tag{7}$$

In practice a factor such as $(1-e^{-r})$ is included in C to make it vanish at $r=0$ without affecting Eq. (7). The functions $\eta_i(r)$ vanish at $r=0$.

In standard variational methods[3] a function is constructed of the form

$$\psi = \phi + S + tC, \tag{8}$$

$$\text{where } \phi = \sum_{i=1}^{n} \eta_i c_i \tag{9}$$

The coefficients c_i are determined by the condition that $(H-E)\,\psi$ should have no components in the space of the functions η_i,

$$(\eta_i|H-E|\psi)=0, \quad i=1,\ldots,n, \tag{10}$$

or

$$\sum_j (\eta_i|H-E|\eta_j)c_j = -(\eta_i|H-E|S+tC), \quad i=1,\ldots,n. \tag{11}$$

It can easily be seen that Eq. (3) is a necessary condition for the existence of a solution of the inhomogeneous system of Eqs. (11) at an eigenvalue E_μ, at which the homogeneous part of Eqs. (11) becomes singular. It follows immediately from this that the Kohn[4] and Hulthén[5] methods and other variational methods which use Eqs. (11), if they give a well-defined value of $t(E)$ for E near E_μ, might be expected to give identical values of t at E_μ. This common limit would be the Harris value

$$t_\mu = -(\phi_\mu|H-E_\mu|S)/(\phi_\mu|H-E_\mu|C), \tag{12}$$

from Eq. (3). In the present paper it will be shown how this result comes about in detail for the Hulthén method, by extending the Harris method to a formalism valid for general values of E. Contrary to expectation, the Kohn method will be shown to lead to a different limiting value of t.

The problem of matching an internal solution ϕ_μ of a potential problem to an external solution $S+tC$

is characteristic of the theory of scattering resonances. A conceptual difficulty arises in the Harris method because ϕ_μ, which is intuitively identified with the internal part of the true wave function ψ, appears to be *orthogonal* to the function ϕ of Eq. (9) as a consequence of the choice of t to satisfy Eq. (3), a necessary condition for the existence of a solution of Eqs. (11). When Eq. (3) is satisfied, an arbitrary multiple of ϕ_μ can be added to ϕ. It will be shown here that the coefficient of ϕ_μ in ψ can be determined by a limiting process as E approaches E_μ. In the Kohn method, this coefficient becomes infinite at E_μ.

In order to carry out this analysis, the Harris method as well as various forms of the standard variational methods are reformulated here as special cases of the theory of resonances.[6] In the course of this analysis, a new method is proposed for treating true resonances and nonresonant scattering within a common formalism. The methods considered here are intended to provide a formalism for scattering theory that as much as possible makes use of techniques developed for stationary-state computations.

II. STANDARD VARIATIONAL METHODS

Following Schwartz,[7] it is convenient to express ψ of Eq. (8) as

$$\psi = (\phi_S + S) + t(\phi_C + C), \tag{13}$$

where $(\eta_i | H - E | \phi_S) = -(\eta_i | H - E | S)$,

$$(\eta_i | H - E | \phi_C) = -(\eta_i | H - E | C), \quad i = 1, \ldots, n. \tag{14}$$

The functions ϕ_S, ϕ_C are expanded in the form of Eq. (9) with coefficients c_i^S, c_i^C, which separately satisfy inhomogeneous equations whose inhomogeneous parts are, respectively, $-(\eta_i | H - E | S)$ and $-(\eta_i | H - E | C)$. Then Eqs. (11) are satisfied identically for all values of the parameter t.

Define the variational functional

$$\mathrm{I}(t) = (\psi | H - E | \psi), \tag{15}$$

$$= M_{00} + (M_{01} + M_{10})\, t + M_{11} t^2, \tag{16}$$

where
$$\left.\begin{aligned} M_{00} &= (S | H - E | \phi_S + S),\\ M_{01} &= (S | H - E | \phi_C + C),\\ M_{10} &= (C | H - E | \phi_S + S),\\ M_{11} &= (C | H - E | \phi_C + C). \end{aligned}\right. \tag{17}$$

Equations (14) have been used in deriving Eq. (16). If H is given by Eq. (5) and S and C by Eqs. (6) and (7), it follows from the fact that ϕ_S and ϕ_C are bounded functions that (in atomic units)

$$M_{01} = M_{10} + \tfrac{1}{2}k\,. \tag{18}$$

For a general value of E in the scattering continuum an exact eigenfunction would satisfy the Schrödinger equation, implying

$$(S | H - E | \psi) = M_{00} + M_{01} t = 0, \quad \text{condition I}, \tag{19}$$

$$(C | H - E | \psi) = M_{10} + M_{11} t = 0, \quad \text{condition II}. \tag{20}$$

When the basis set η_i is incomplete, these two conditions in general are incompatible. If used to determine t, the tangent of the phase shift, they would give two different values

$$t_{\mathrm{I}} = -M_{00}/M_{01}, \tag{21}$$

$$t_{\mathrm{II}} = -M_{10}/M_{11}. \tag{22}$$

The function $I(t)$ given by Eq. (16) is a linear combination of Eqs. (19) and (20). The Hulthén variational method[5] determines t as a root of the quadratic equation

$$I(t) = M_{00} + (M_{01} + M_{10})t + M_{11} t^2 = 0. \tag{23}$$

From Eqs. (16) and (18) and from the fact that M_{00}, etc., are independent of the parameter t, it follows that

$$\partial I / \partial t = \tfrac{1}{2}k + 2(M_{10} + M_{11} t) \tag{24}$$

and
$$\partial (I t^{-2}) / \partial (t^{-1}) = -\tfrac{1}{2}k + 2(M_{01} + M_{00} t^{-1}). \tag{25}$$

For an exact eigenfunction, or more generally, from Eq. (20) if t is equal to t_{II} of Eq. (22),

$$\partial I / \partial t = \tfrac{1}{2}k, \quad \text{if } t = t_{\mathrm{II}}. \tag{26}$$

Similarly, from Eqs. (19), (21), and (25),

$$\partial (I t^{-2}) / \partial (t^{-1}) = -\tfrac{1}{2}k, \quad \text{if } t = t_{\mathrm{I}}. \tag{27}$$

It follows from Eq. (26) that

$$t_K = t_{\mathrm{II}} - (2/k) I(t_{\mathrm{II}}) \tag{28}$$

is stationary within the constraints imposed by choice of a basis set η_i. Equation (28) is used to determine t in the method of Kohn.[4] An analogous result holds for

$$t_R^{-1} = t_{\mathrm{I}}^{-1} + (2/k) I(t_{\mathrm{I}}) t_{\mathrm{I}}^{-2} \tag{29}$$

as a consequence of Eq. (27).[8]

Some insight into the significance of Eq. (28) can be gained by recognizing that it is equivalent to making a linear extrapolation from t_{II} to the Hulthén value of t, for which $I(t)$ vanishes. This gives, from Eq. (26),

$$0 = I(t) = I(t_{\mathrm{II}}) + \tfrac{1}{2}k(t - t_{\mathrm{II}}). \tag{30}$$

Hence, making use of Eq. (20),

$$\begin{aligned} t_K &= t_{\mathrm{II}} - (2/k) I(t_{\mathrm{II}})\\ &= t_{\mathrm{II}} - (2/k)(M_{00} + M_{01} t_{\mathrm{II}})\\ &= -(M_{10}/M_{11}) - (2/kM_{11})\det M, \end{aligned} \tag{31}$$

where
$$\det M = M_{00} M_{11} - M_{01} M_{10}\,. \tag{32}$$

For comparison, the Hulthén value of t can be expressed by

$$t_H = -\frac{M_{10}}{M_{11}} + \frac{k}{4M_{11}}\left[\left(1 - \frac{16}{k^2}\det M\right)^{1/2} - 1\right], \tag{33}$$

from Eqs. (18) and (23). Obviously Eq. (31) is the linear term in a power series expansion of Eq.

(33) in powers of $\det M$. The two equations coincide when $\det M$ vanishes, as it does whenever t_{I} and t_{II}, given, respectively, by Eqs. (21) and (22 (22), are equal.

Equation (29) can also be shown to be a linear approximation to the Hulthén value of t, starting from t_{I}. From Eq. (19),

$$t_R^{-1}=t_{\mathrm{I}}^{-1}+(2/k)(M_{10}t_{\mathrm{I}}^{-1}+M_{11})$$

$$=-(M_{01}/M_{00})+(2/kM_{00})\det M. \tag{34}$$

The Hulthén value can be expressed in the form

$$t_H^{-1}=-\frac{M_{01}}{M_{00}}-\frac{k}{4M_{00}}\left[\left(1-\frac{16}{k^2}\det M\right)^{1/2}-1\right]. \tag{35}$$

Equation (34) is a linear approximation to the expansion of Eq. (35) in powers of $\det M$.

It can easily be shown that an attempt to use both t_{I} and t_{II} in a linear extrapolation formula leads again to the Kohn formula, Eq. (31) or to Eq. (34). Since

$$I(t_{\mathrm{I}})=(M_{00}/M_{01}^2)\det M,$$

$$\text{and } I(t_{\mathrm{II}})=M_{11}^{-1}\det M, \tag{36}$$

the linear extrapolation formula gives, from Eqs. (21), (22), and (36),

$$t=[I(t_{\mathrm{I}})t_{\mathrm{II}}-I(t_{\mathrm{II}})t_{\mathrm{I}}]/[I(t_{\mathrm{I}})-I(t_{\mathrm{II}})]=t_R \tag{37}$$

or

$$t^{-1}=\frac{I(t_{\mathrm{I}})t_{\mathrm{I}}^{-2}t_{\mathrm{II}}^{-1}-I(t_{\mathrm{II}})t_{\mathrm{II}}^{-2}t_{\mathrm{I}}^{-1}}{I(t_{\mathrm{I}})t_{\mathrm{I}}^{-2}-I(t_{\mathrm{II}})t_{\mathrm{II}}^{-2}}=t_K^{-1}. \tag{38}$$

III. THE HARRIS METHOD

The eigenvectors of Eq. (2) lead to orthonormal functions

$$\phi_\alpha=\sum_{i=1}^{n}\eta_i c_i^\alpha,\quad \alpha=1,\dots,n. \tag{39}$$

The ϕ_α are eigenfunctions of H within the Hilbert space spanned by the basis functions η_i. In particular, the functions ϕ_S and ϕ_C of Eq. (14) can be expanded in terms of the ϕ_α and the eigenvalues E_α,

$$\phi_S=\sum_{\alpha=1}^{n}\phi_\alpha(E-E_\alpha)^{-1}M_{\alpha S},$$

$$\phi_C=\sum_{\alpha=1}^{n}\phi_\alpha(E-E_\alpha)^{-1}M_{\alpha C}, \tag{40}$$

where
$$M_{\alpha S}=(\phi_\alpha|H-E|S),$$
$$M_{\alpha C}=(\phi_\alpha|H-E|C). \tag{41}$$

The matrix elements defined by Eq. (17) can be expressed as

$$M_{00}=M_{SS}+\Sigma_\alpha M_{S\alpha}(E-E_\alpha)^{-1}M_{\alpha S},$$

$$M_{01}=M_{SC}+\Sigma_\alpha M_{S\alpha}(E-E_\alpha)^{-1}M_{\alpha C},$$

$$M_{10}=M_{CS}+\Sigma_\alpha M_{C\alpha}(E-E_\alpha)^{-1}M_{\alpha S}, \tag{42}$$

$$M_{11}=M_{CC}+\Sigma_\alpha M_{C\alpha}(E-E_\alpha)^{-1}M_{\alpha C},$$

where $M_{SS}=(S|H-E|S)$, etc. (43)

As E approaches E_μ, an eigenvalue of Eq. (2),

$$(E-E_\mu)M_{00}\rightarrow M_{S\mu}M_{\mu S},$$

$$(E-E_\mu)M_{01}\rightarrow M_{S\mu}M_{\mu C},$$

$$(E-E_\mu)M_{10}\rightarrow M_{C\mu}M_{\mu S}, \tag{44}$$

$$(E-E_\mu)M_{11}\rightarrow M_{C\mu}M_{\mu C}.$$

The matrix of M is Hermitian whenever one index refers to a normalizable function such as ϕ_μ. It follows from this that Eqs. (21) and (22) become identical in the limit indicated by Eq. (44):

$$t_{\mathrm{I}}(E_\mu)=t_{\mathrm{II}}(E_\mu)=-M_{\mu S}/M_{\mu C}, \tag{45}$$

for matrix elements evaluated at E_μ. This limit is equal to t_μ as determined by Eq. (3), equivalent to

$$M_{\mu S}(E_\mu)+M_{\mu C}(E_\mu)t_\mu=0. \tag{46}$$

The Hulthén condition, Eq. (23), becomes

$$M_{\mu S}^2+2M_{\mu S}M_{\mu C}t+M_{\mu C}^2t^2$$

$$=(M_{\mu S}+M_{\mu C}t)^2=0, \tag{47}$$

equivalent to Eq. (46).

From Eqs. (40) and (44) it follows that the limit of the function ϕ, in Eq. (8), as E approaches E_μ and t approaches t_μ, is

$$\phi\rightarrow\sum_{\alpha\neq\mu}\phi_\alpha(E_\mu-E_\alpha)^{-1}[M_{\alpha S}(E_\mu)+M_{\alpha C}(E_\mu)t_\mu]$$

$$+\phi_\mu(\partial/\partial E)[M_{\mu S}(E)+M_{\mu C}(E)\,t(E)]\,|_{E_\mu}. \tag{48}$$

IV. RESONANCE FORMALISM

Several of the expressions for the tangent of the phase shift considered here can be put into the form

$$t=\{-\tfrac{1}{2}\Gamma_\mu(E)/[E-E_\mu-\Delta_\mu(E)]\}, \tag{49}$$

where, in general, the functions Γ_μ and Δ_μ have nonzero values at $E=E_\mu$. If $\Delta_\mu(E_\mu)$ is small, t has a pole near E_μ, and Eq. (49) is a form of Breit-Wigner formula. This formula describes a scattering resonance unless Γ_μ vanishes at the pole.[6] The width of the resonance is given by $\Gamma_\mu(E_\mu)$ if Δ_μ is small. The usual potential-scattering contribution to the resonance formula for t occurs in Eq. (49) through the energy dependence of the functions $\Gamma_\mu(E)$ and $\Delta_\mu(E)$. The Feshbach theory of resonant scattering[6] can be adapted to the present analysis if the interior space Q is identified with the finite dimensional space spanned by the basis functions η_i. The external space P contains only the functions S and C, orthogonalized to the η_i, or equivalently, to the eigenfunctions ϕ_α. At a given energy E, the Green's function used in the Feshbach theory must be replaced by some approximate solution of the two Eqs. (19) and (20), which are in general incompatible. This brings the theory back to the standard dilemma of all finite variational methods, and an arbitrary choice of methods must be made.

It will be shown in the following section that the Hulthén value of the tangent of the phase shift does not vary smoothly in the immediate neighborhood of an eigenvalue E_μ of Eq. (2). This is due to a pole in $\det M$, which leads to two closely spaced branch points in t_H. In contrast, the Kohn[4] or Rubinow[8] formulas, Eqs. (28) or (29), respectively, do not have singularities at E_μ. Either the Hulthén or Rubinow methods, introduced at this point in the Feshbach formalism, lead to an expression for t equivalent to Eq. (49), where E_μ is an eigenvalue of Eqs. (2).

By use of Eq. (18), Eq. (34) can be written in the form

$$\begin{aligned} t_R &= -M_{00}/(M_{01}-2k^{-1}\det M) \\ &= 2k^{-1}(E-E_\mu)M_{00} \\ &\quad\times[E-E_\mu+2k^{-1}(E-E_\mu)(M_{10}-2k^{-1}\det M)]^{-1} \\ &= -\tfrac{1}{2}\Gamma_\mu(E)/[E-E_\mu-\Delta_\mu(E)], \end{aligned} \tag{50}$$

where $$\Gamma_\mu(E)=4k^{-1}(E-E_\mu)M_{00} \tag{51}$$

and $$\Delta_\mu(E)=-2k^{-1}(E-E_\mu)(M_{10}-2k^{-1}\det M). \tag{52}$$

Both of these functions have nonzero limits as E approaches E_μ. It will be shown in the following section that $\det M$ has a simple pole at E_μ, of the form $D_\mu^{(1)}(E-E_\mu)^{-1}$. Then, by Eqs. (42), as E approaches E_μ,

$$\Gamma_\mu(E)\to 4k^{-1}M_{S\mu}M_{\mu S}, \tag{53}$$

$$\Delta_\mu(E)\to -2k^{-1}[M_{C\mu}M_{\mu S}-2k^{-1}D_\mu^{(1)}]\ . \tag{54}$$

The limiting value of $\Gamma_\mu(E)$ is non-negative, as it must be for Γ_μ to be identified with the width of a resonant energy level. The limiting value of t is

$$\begin{aligned} t_R &\to \tfrac{1}{2}\Gamma_\mu(E_\mu)/\Delta_\mu(E_\mu) \\ &= -M_{S\mu}/[M_{C\mu}-2k^{-1}D_\mu^{(1)}/M_{\mu S}]. \end{aligned} \tag{55}$$

This differs from the Harris value t_μ unless $D_\mu^{(1)}$ vanishes.

The Hulthén formula, Eq. (35), can also be expressed in the Breit-Wigner form, Eq. (50), with

$$\Gamma_\mu(E)=4k^{-1}(E-E_\mu)M_{00} \tag{56}$$

and $$\begin{aligned}\Delta_\mu(E) &= -2k^{-1}(E-E_\mu)\{M_{10} \\ &\quad+\tfrac{1}{4}k[(1-16k^{-2}\det M)^{1/2}-1]\}\ . \end{aligned} \tag{57}$$

As E approaches E_μ,

$$\Gamma_\mu(E)\to 4k^{-2}M_{S\mu}M_{\mu S}\ , \tag{58}$$

$$\Delta_\mu(E)\to -2k^{-1}M_{C\mu}M_{\mu S}\ , \tag{59}$$

and $$t_H\to -M_{S\mu}/M_{C\mu}\ , \tag{60}$$

equal to the Harris value t_μ.

Equations (50) – (52) or (57) provide a common formalism for computations of resonant and nonresonant scattering. The Harris method is characterized by the introduction of a *pseudoresonance*, at the energy E_μ, which in general is a pure artifact of the computation, depending on an arbitrary choice of the basis function set η_i. Such a pseudoresonance will have values of Γ_μ and Δ_μ with a finite ratio, t_μ, the tangent of the phase shift. The eigenvalue E_μ, which has no physical significance, will not approach a definite limit.

In contrast, at a physical resonance, the eigenvalue E_μ can be expected to approach a definite limit as the set η_i approaches completeness, as in calculations by Taylor and Williams[9] and by Miller,[6] equivalent to the solution of Eq. (2). This characteristic behavior could be used in practical computations to distinguish between physical resonances and pseudoresonances.

V. BEHAVIOR NEAR A PSEUDORESONANCE

Illustrative calculations of the S-wave phase shift δ_0 were carried out for the potential function

$$V(r)=-e^{-r} \tag{61}$$

with basis functions of the form

$$\eta_i=r^i e^{-2.5r}\ ,\quad i=1,\ldots,n. \tag{62}$$

TABLE I. Tangent of the phase shift for k near k_μ.

			$n=4$ $k_\mu=0.492\,078$ $E_\mu=0.121\,070$		
k	0.482 078	0.487 078	0.492 078	0.497 078	0.502 078
$t_{\mathrm{I}}{}^{a}$	2.744 32	2.685 26		2.575 61	2.524 65
$t_{\mathrm{II}}{}^{b}$	2.736 13	2.681 51		2.578 80	2.530 55
$t_K{}^{c}$	2.847 03	2.783 96		2.667 06	2.612 79
$t_H{}^{d}$	2.845 17^{g}	2.732 46^{g}		2.633 63	2.591 15
$t_R{}^{e}$	2.851 36	2.787 87	2.727 60	2.670 31	2.615 76
$t_H{}^{f}$	2.849 49^{g}	2.735 33^{g}	2.629 09	2.633 63	2.591 15
			$n=6$ $k_\mu=0.263\,984$ $E_\mu=0.034\,843\,7$		
k	0.253 984	0.258 984	0.263 984	0.268 984	0.273 984
$t_{\mathrm{I}}{}^{a}$	-7.919 18	-8.973 69		-12.0816	-14.5129
$t_{\mathrm{II}}{}^{b}$	-7.886 43	-8.947 90		-12.1671	-14.9348
$t_K{}^{c}$	-7.731 54	-8.733 71		-11.6461	-13.8725
$t_H{}^{d}$	-7.708 55	-8.625 94		-11.7271	-13.9676
$t_R{}^{e}$	-7.735 14	-8.739 30	-10.0084	-11.6641	-13.9162
$t_H{}^{f}$	-7.708 56	-8.625 94	-10.3152	-11.7271	-13.9676
			$n=8$ $k_\mu=0.759\,688$ $E_\mu=0.288\,563$		
k	0.749 688	0.754 688	0.759 688	0.764 688	0.769 688
$t_{\mathrm{I}}{}^{a}$	1.396 19	1.384 94		1.363 15	1.352 69
$t_{\mathrm{II}}{}^{b}$	1.397 17	1.385 44		1.362 63	1.351 60
$t_K{}^{c}$	1.389 51	1.377 74		1.354 89	1.343 79
$t_H{}^{d}$	1.389 78	1.378 27		1.354 04	1.343 38
$t_R{}^{e}$	1.389 55	1.377 78	1.366 25	1.354 93	1.343 84
$t_H{}^{f}$	1.389 78	1.378 27	1.373 93	1.354 04	1.343 38

[a] See Eq. (21).
[b] See Eq. (22).
[c] See Eq. (31).
[d] See Eq. (33).
[e] See Eq. (33).
[f] See Eq. (34) or (55).
[g] Root of Eq. (23) is complex. Value in table is real part of root.

Results for values of k near k_μ, corresponding to a pseudoresonance eigenvalue E_μ, were calculated for $n=4$, 6, and 8. In each case only one value of k_μ lies in the range $0.1 \leq k_\mu \leq 1.0$. The tangent of the phase shift computed by several different methods is given in Table I.

The values of the tangent of the Hulthén phase shift in Table I do not vary smoothly about t_μ. This is due to the analytic behavior of det$M$, which is singular at E_μ. From Eqs. (42), each of the coefficients M_{00}, etc., has a simple pole at E_μ. In det$M$, the quadratic term has the coefficient

$$D_\mu{}^{(2)}=M_{S\mu}M_{\mu S}M_{C\mu}M_{\mu C}-M_{S\mu}M_{\mu C}M_{C\mu}M_{\mu S}\equiv 0, \tag{63}$$

so det$M$ also has a simple pole at E_μ,

$$\det M=D_\mu{}^{(1)}(E-E_\mu)^{-1}+D_\mu{}^{(0)}+\cdots. \tag{64}$$

It follows from this that the argument of the square root in Eq. (33) or (35) vanishes at some point $E_\mu{}'$, near E_μ, where

TABLE II. Values of k_μ, E_μ, and $k_\mu{}'$, $E_\mu{}'$ in range $0 < k < 1.0$.

n	k_μ	E_μ	$k_\mu{}'$	$E_\mu{}'$
4	0.492 08	0.121 07	0.471 25	0.111 04
6	0.263 98	0.034 84	0.259 53	0.033 68
8	0.759 69	0.288 56	0.761 40	0.289 87

$$\det M(E_\mu{}') = \tfrac{1}{16}k^2. \tag{65}$$

The argument of the square root is negative between $E_\mu{}'$ and E_μ, and t_H is complex in this interval. Values of E_μ and $E_\mu{}'$, and the corresponding values of k, are given in Table II. For $n=4$, two of the values of k considered in Table I fall within this interval. The real part of t_H is tabulated.

If $E_\mu{}'$ is less than E_μ, Eq. (33) shows that $t(E)$ is of the form

$$t_H(E) = t_\mu + t_\mu{}^{(1/2)}(E - E_\mu)^{1/2} + t_\mu{}^{(1)}(E - E_\mu) + \cdots \tag{66}$$

for $E > E_\mu$, or

$$t_H(E) = t_\mu{}' + t_\mu{}^{(1/2)\prime}(E_\mu{}' - E)^{1/2} + t_\mu{}^{(1)\prime}(E_\mu{}' - E) + \cdots, \tag{67}$$

for $E < E_\mu{}'$. Because of the branch points at E_μ and $E_\mu{}'$, t_H is not a smooth function of E or k in this region, despite the fact that a well-defined limit, t_μ, exists at E_μ.

The coefficient $D_\mu{}^{(1)}$ in Eq. (64) can be written down from substitution of Eqs. (42) into Eq. (32). It does not vanish in general, but it consists of terms of the form of finite quantities multiplied by quadratic products of the integrals $M_{\mu S}$ or $M_{\mu C}$, given by Eq. (41). As the basis set of normalizable functions used in the calculations goes to completeness, these integrals should vanish, because the function ϕ_μ must become an increasingly good approximation to an eigenfunction of $H - E$. In this sense, the pole of $\det M$ is an artifact of the computation, due to incompleteness of the basis set. Some evidence of this can be seen from the values of E_μ and $E_\mu{}'$ listed in Table II. The interval between the two, a measure of the strength of the pole of $\det M$ at E_μ, decreases rapidly as n is increased.

While the effect of the pole at E_μ is most striking in the interval between $E_\mu{}'$ and E_μ, where t_H becomes complex, there is also a distortion for

TABLE III. Tangent of the phase shift for k near k_μ, with smoothing constants C = 1.0, 0.5, and 0.1.

		$n=4$	$k_\mu = 0.492\,078$ $E_\mu = 0.121\,070$		
k	0.482 078	0.487 078	0.492 078	0.497 078	0.502 078
t^{a}	2.849 49[e]	2.735 33[e]	2.629 09	2.633 63	2.591 15
t^{b}	2.849 49[e]	2.735 33[e]	2.629 09	2.595 03[e]	2.562 78[e]
t^{c}	2.774 31[e]	2.699 73[e]	2.629 09	2.586 11[e]	2.545 20[e]
t^{d}	2.749 53[e]	2.687 78[e]	2.629 09	2.577 89[e]	2.529 08[e]
		$n=6$	$k_\mu = 0.263\,984$ $E_\mu = 0.034\,843\,7$		
k	0.253 984	0.258 984	0.263 984	0.268 984	0.273 984
t^{a}	-7.708 55	-8.625 94	-10.315 2	-11.727 1	-13.967 6
t^{b}	-7.708 55	-8.625 94	-10.315 2	-11.727 1	-13.967 6
t^{c}	-7.708 55	-8.818 16[e]	-10.315 2	-11.862 8[e]	-13.967 6
t^{d}	-7.876 45[e]	-8.946 05[e]	-10.315 2	-12.033 4[e]	-14.373 6[e]
		$n=8$	$k_\mu = 0.759\,688$ $E_\mu = 0.288\,563$		
k	0.749 688	0.754 688	0.759 688	0.764 688	0.769 688
t^{a}	1.389 78	1.378 27	1.373 93	1.354 04	1.343 39
t^{b}	1.389 78	1.378 27	1.373 93	1.354 04	1.343 39
t^{c}	1.389 78	1.378 27	1.373 93	1.354 04	1.343 39
t^{d}	1.391 83[e]	1.382 73[e]	1.373 93	1.360 77[e]	1.347 85[e]

[a] Equation (35), real part only.
[b] Equations (35), (68), C = 1.0.
[c] Equations (35), (68), C = 0.5.
[d] Equations (35), (68), C = 0.1.
[e] Smoothed value.

TABLE IV. Width parameter $\Gamma_\mu(k)$ and shift parameter $\Delta_\mu(k)$ for k near k_μ, $n=6$ only.

k	0.253 984	0.258 984	0.263 984	0.268 984	0.273 984
Γ_μ[a]	0.193 983	0.194 834	0.195 551	0.196 132	0.196 576
Δ_μ[b]	-0.015 129	-0.012 455	-0.009 769	-0.007 075	-0.004 373
Δ_μ[c]	-0.015 172	-0.012 601	-0.009 479	-0.007 030	-0.004 347
Δ_μ[d]	-0.015 172	-0.012 601	-0.009 479	-0.007 030	-0.004 347
Δ_μ[e]	-0.015 172	-0.012 355[g]	-0.009 479	-0.006 934[g]	-0.004 347
Δ_μ[f]	-0.014 904[g]	-0.012 197[g]	-0.009 479	-0.006 817[g]	-0.004 148[g]

[a] See Eq. (51).
[b] See Eq. (52).
[c] See Eq. (57), real part only.
[d] See Eqs. (57), (68), C = 1.0.
[e] See Eqs. (57), (68), C = 0.5.
[f] See Eqs. (57), (68), C = 0.1.
[g] Smoothed value.

$E > E_\mu$, if $E_\mu' < E_\mu$, indicated by the square-root term in Eq. (66). Merely replacing t_H by its real part is not a consistent procedure, because it amounts to truncating the pole term in det$M$ on one side of E_μ while retaining it on the other. This suggests the use of a smoothing formula, replacing the argument of the square root in Eq. (33) or (35) by a function

$$f(E) = 1 - 16k^{-2}\det M(E), \quad |\det M| \leq \tfrac{1}{16}k^2 C,$$
$$= 1 - C\,\mathrm{sgn}(\det M), \quad |\det M| > \tfrac{1}{16}k^2 C, \qquad (68)$$

where the smoothing parameter C lies in the range $0 \leq C \leq 1$. The replacement of t_H by its real part is equivalent to using $C = 1$ when det$M$ is positive, but allowing C to be infinite when det$M$ is negative.

Results of calculations with values of $C = 1.0$, 0.5, and 0.1 are given in Table III. As the dimension n of the basis set is increased, the effect of smoothing becomes less important. Values of the width and shift parameters, computed from Eqs. (51), (52), (57), and (68), are given in Table IV. The effect of smoothing and of the $D_\mu^{(1)}$ term in Eq. (54) can be seen in Δ_μ.

Equations (44) and (64) can be used to derive the limiting value of t_K, Eq. (31), as E approaches E_μ. This is

$$t_K \to -[M_{C\mu}M_{\mu S} + 2k^{-1}D_\mu^{(1)}]/M_{C\mu}M_{\mu C}. \qquad (69)$$

This limit is different from Eq. (55) or Eq. (60). The three become identical only when $D_\mu^{(1)}$ vanishes.

VI. BEHAVIOR NEAR ZEROES OF M_{00} OR M_{11}

In addition to the irregular behavior of $t(E)$ near E_μ, Eqs. (31) and (34) indicate that t_K and t_R^{-1} have poles at the zeroes, respectively, of M_{11} and M_{00}. Values of t computed by several different methods in the neighborhood of such zeroes are given in Table V. The computed value of t_K shows wild fluctuations near a zero of M_{11}, while, somewhat surprisingly, t_R appears to remain smooth near a zero of M_{00}. The fact that Eqs. (33) and (35) for t_H are formally identical shows that the apparent pole at a zero of M_{11} or M_{00}, respectively, is not real, and the Hulthén phase shifts remain smooth functions near such points.

Because the apparent pole in Eq. (33) or (35) is nullified by an exact cancellation between the two terms in either formula, in general one of these formulas should be used in preference to the other for numerical accuracy. A reasonable criterion would be to use Eq. (33) when $|M_{00}/M_{11}| < 1$ and Eq. (35) when $|M_{00}/M_{11}| > 1$.

The present work indicates that the fluctuations in t_K studied by Schwartz[7] are due to the occurrence of zeroes of M_{11} rather than to singularities of Eqs. (11) at eigenvalues E_μ. Fluctuations due to zeroes of M_{11} can probably be avoided by judicious use of the Rubinow or Hulthén formulas.

VII. CONCLUSIONS

Recent calculations by Morawitz[10] indicate that for small basis sets, the Kohn phase shift computed at a pseudoresonance E_μ is in somewhat better agreement with the exact value (computed for an exponential or Yukawa potential) than is the Hulthen phase shift. The Kohn or Rubinow phase shifts, from the results given in Table I, are in good agreement with each other near a pseudoresonance E_μ, where they approach limits differing significantly from the Harris phase shift. It can be concluded that t_K or t_R should be computed in preference to t_H near a pseudoresonance.

In contrast to this, the Hulthén formula has the advantage of nonsingular behavior near zeroes of M_{00} and M_{11}, where the formulas for t_R and t_K have vanishing denominators. For numerical accuracy, t_K, Eq. (31), or t_H, Eq. (33) should be used

Table V. Tangent of the phase shift near zeroes of M_{00} or M_{11}.
Calculations for $n=6$ only.

k	0.281 00	0.281 01	0.281 02	0.281 03
M_{11}	14.592×10^{-6}	5.212×10^{-6}	-3.424×10^{-6}	-11.805×10^{-6}
t_I[a]	−20.0225	−20.0338	−20.0445	−20.0548
t_{II}[b]	−585.685	−1606.15	2395.84	680.891
t_K[c]	14.3845	74.4587	−161.069	−60.1516
t_H[d]	−18.9756	−18.9932	−18.9622	−18.9924
t_R[e]	−18.9115	−18.9206	−18.9302	−18.9395
t_H[f]	−18.9700	−18.9792	−18.9889	−18.9981
k	0.569 17	0.569 18	0.569 19	0.569 20
M_{00}	20.802×10^{-6}	6.676×10^{-6}	-6.974×10^{-6}	-19.133×10^{-6}
t_I[a]	2.814 52	−37.3333	0.966 942	1.479 26
t_{II}[b]	2.073 90	2.073 85	2.073 79	2.073 73
t_K[c]	2.073 88	2.073 82	2.073 77	2.073 70
t_H[d]	2.073 88	2.073 82	2.073 77	2.073 70
t_R[e]	2.073 89	2.073 85	2.073 73	2.073 69
t_H[f]	2.072 50	2.071 76	2.074 58	2.075 35
k	0.874 64	0.874 65	0.874 66	0.874 67
M_{11}	27.001×10^{-6}	1.240×10^{-6}	-1.216×10^{-6}	-26.524×10^{-6}
t_I[a]	1.146 96	1.146 96	1.146 94	1.146 93
t_{II}[b]	55.521	119.317	−119.343	−53.9528
t_K[c]	1.333 36	1.546 72	0.747 07	0.966 60
t_H[d]	1.150 91	1.151 29	1.150 88	1.150 39
t_R[e]	1.150 83	1.150 81	1.150 79	1.150 78
t_H[f]	1.150 84	1.150 82	1.150 81	1.150 79

[a] See Eq. (21).
[b] See Eq. (22).
[c] See Eq. (31).
[d] See Eq. (33).
[e] See Eq. (34).
[f] See Eq. (35).

when M_{00}/M_{11} is small, and t_R, Eq. (34) or t_H, Eq. (35) should be used when M_{00}/M_{11} is large.

ACKNOWLEDGMENTS

The author is indebted to H. Morawitz for the FORTRAN program used to evaluate matrix elements required in this work. The calculations were carried out on the CALL/360 terminal system, with programs rewritten in the BASIC language for a trial of this system. The author is indebted for helpful conversations to H. Morawitz, F. E. Harris, H. H. Michels, H. S. Taylor, and C. Schwartz.

[1] F. E. Harris, Phys. Rev. Letters 19, 173 (1967).

[2] H. H. Michels and F. E. Harris, Phys. Rev. Letters 19, 885 (1967).

[3] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, New York, 1965), pp. 111–118.

[4] W. Kohn, Phys. Rev. 74, 1763 (1948).

[5] L. Hulthén, Kgl. Fysiograf. Sällskap. Lund Forh. 14, No. 21 (1944).

[6] H. Feshbach, Ann. Phys. (N. Y.) 19, 287 (1962); 43, 410 (1967); T. F. O'Malley and S. Geltman, Phys. Rev. 137, A1344 (1965); W. H. Miller, *ibid.* 152, 70 (1966); H. S. Taylor, G. V. Nazaroff, and A. Golebiewski, J. Chem. Phys. 45, 2872 (1966).

[7] C. Schwartz, Ann. Phys. (N. Y.) 16, 36 (1961); Phys. Rev. 124, 1468 (1961).

[8] L. Hulthén, Arkiv. Mat. Astron. Fys. 35A, No. 25 (1948); S. I. Rubinow, Phys. Rev. 98, 183 (1955); K. L. Williams, Proc. Phys. Soc. (London) 91, 807 (1967).

[9] H. S. Taylor and J. K. Williams, J. Chem. Phys. 42, 4063 (1965).

[10] H. Morawitz, to be published.

PHYSICAL REVIEW VOLUME 175, NUMBER 1 5 NOVEMBER 1968

Polarization of Light from Collision of a Proton Beam with Helium Atoms*

Daniel Krause, Jr., and Edward A. Soltysik
University of Massachusetts, Amherst, Massachusetts

(Received 9 May 1968)

We have measured the relative cross-sections and the polarization of the light resulting from the excitation of helium by a proton beam for the following transitions:

$3\ ^1D \rightarrow 2\ ^1P$ ($\lambda = 6678$ Å), $3\ ^1S \rightarrow 2\ ^1P$ ($\lambda = 7281$ Å),
$3\ ^3D \rightarrow 2\ ^3P$ ($\lambda = 5876$ Å), $3\ ^3S \rightarrow 2\ ^3P$ ($\lambda = 7065$ Å).

Our analysis indicates that there is a small violation of the $\Delta S = 0$ spin rule for the excitation of the $3\ ^3D$ and $3\ ^3S$ states of helium by protons.

INTRODUCTION

When a beam of particles passes through a volume of space containing ground-state helium atoms, some of the beam particles undergo inelastic collisions with the target-gas atoms, resulting in the excitation of the atoms. Subsequent to excitation by the beam, the helium atom may de-excite to a lower state, with the emission of a photon. This photon is characterized by its wavelength and the direction of its electric field with respect to the beam direction. If, as a result of collisions between beam particles and target-gas atoms, there is an unequal population of the rotationally degenerate substates associated with a given energy of the excited atoms, then there is a net orientation imparted to the excited atoms. This is manifested by the emission of polarized light when the atoms de-excite. The degree of polarization[1] is determined by the collision cross sections for transitions to the various rotationally degenerate substates associated with a given energy configuration.

A number of experimenters[2-4] have in recent years measured the relative excitation cross section and the polarization of light resulting from the excitation of helium by an electron beam. Special emphasis has been given to the electron energy-threshold region for the excitation of some states in helium, where simple consideration of conservation of angular momentum leads to a unique prediction of the value of the polarization. Careful experimental work in the region of the electron-energy threshold has shown that, in general, very close to threshold, the measured polarization is in reasonable agreement with theoretical predictions.

The relative excitation cross sections for protons, deuterons, and neutral hydrogen atoms on helium have been measured by a number of investigators[5-8] for a number of states of helium at various energies. Van Eck, de Heer, and Kistemaker[6] At Amsterdam have measured both the excitation cross section and polarization for a number of helium states excited by protons and neutral hydrogen atoms in the energy range 5 keV $<E<$ 150 keV. In addition, for a rather complete discussion and list of references on the excitation of some helium states by protons and the polarization of the emitted light, the reader is referred to the doctoral thesis of Van Den Bos.[7] Much of the work of the Amsterdam group is given in this thesis.

It was the purpose of the work reported here to measure the relative cross section and the polarization of the radiation resulting from the excitation of the $n = 3$ states of helium by proton impact in the low-beam-energy region. In particular, we concentrated our efforts on the $l = 0$ and $l = 2$ states for the following two reasons: 1. The line radiation from these states is widely separated from any other lines; thus we could be absolutely sure that our narrow band-pass filters would properly exclude radiation from other states. This is particularly important at low beam energies where the light intensity is very weak. 2. There is a lack of data on the polarization of light for these states in the low-beam-energy region.

In this work, we measured the intensity and