Electron scattering from excited states of hydrogen: Implications for the ionization threshold law

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The elastic scattering wave function for electrons scattered from the Nth excited state of hydrogen is the final state of the matrix element for excitation of that state. This paper deals with the solution of that problem primarily in the context of the Temkin-Poet (TP) model [A. Temkin, Phys. Rev. **126**, 130 (1962); R. Poet, J. Phys. B **11**, 3081 (1978)], wherein only the radial parts of the interaction are included. The relevant potential for the outer electron is dominated by the Hartree potential, $V_N^{\mathrm{H}}(r)$. In the first part of the paper, $V_N^{\mathrm{H}}(r)$ is approximated by a potential $W_N(r)$, for which the scattering equation can be analytically solved. The results allow formal analytical continuation of N into the continuum, so that the ionization threshold law can be deduced. Because the analytic continuation involves going from N to an imaginary function of the momentum of the inner electron, the threshold law turns out to be an exponentially damped function of the available energy E, in qualitative accord with the result of Macek and Ihra [J. H. Macek and W. Ihra, Phys. Rev. A **55**, 2024 (1997)] for the TP model. Thereafter, the scattering equation for the Hartree potential $V_N^{\mathrm{H}}(r)$ is solved numerically. The numerical aspects of these calculations have proven to be challenging and required several developments for the difficulties to be overcome. The results for $V_N^{\mathrm{H}}(r)$ show only a simple energy-dependent shift from the approximate potential $W_N(r)$, which therefore does not change the analytic continuation and the form of the threshold law. It is concluded that the relevant optical potential must be included in order to compare directly with the analytic result of Macek and Ihra. The paper concludes with discussions of (a) a quantum mechanical interpretation of the result, and (b) the outlook of this approach for the complete problem.

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I. INTRODUCTION

The elastic scattering wave function of electrons from the Nth excited s state of hydrogen is governed by the equation (in Rydberg units, used throughout unless explicitly stated)

$$\left[-\nabla_1^2 + PHP + V_N^{(\mathrm{opt})} - k_N^2\right] U_N(\mathbf{r}_1) = 0. \qquad (1.1)$$

In principle P is the Feshbach projection operator which includes all open channels.

In practice, however, PHP is replaced by the term coming from the Nth state alone, in which case, not including exchange,

$$P = \phi_{N0}(r_2)\rangle\langle\phi_{N0}(r_2), \qquad (1.2)$$

where $\phi_{N0}(r)$ is the Nth s state of the hydrogen atom, so that PHP goes into V_N^{H}, the Hartree potential of the Nth state [cf. Eq. (1.5)]. $V_N^{(\mathrm{opt})}$ is the relevant optical potential [1], and k_N^2 is the energy of the emerging electron after the target (hydrogen) has been excited to the Nth excited state. The total energy of the system, E, is thus

$$E = k_N^2 - \frac{1}{N^2}. \qquad (1.3)$$

In this paper we use the Temkin-Poet (TP) model [2,3], which is defined by including only purely radial correlations in the interaction. Thus the vector $\mathbf{r}$ becomes the radial scalar r, and the electron-electron repulsion becomes

$$\frac{2}{r_{12}} \to \frac{2}{r_>(1,2)}, \qquad (1.4)$$

where $r_>(1,2)$ is the larger of r_1 or r_2. The potential for the scattered electron is dominated by the Hartree potential.

$$V_N^{\mathrm{H}}(r_1) = \langle\varphi_{N0}(r_2)| -\frac{2}{r_1} + \frac{2}{r_>(1,2)} |\varphi_{N0}(r_2)\rangle, \qquad (1.5)$$

so that the equation we shall actually be dealing with here can be reduced to the form

$$\left[-\frac{d^2}{dr_1^2} + V_N^{\mathrm{H}}(r_1) - k_N^2\right] u_N^{\mathrm{H}}(r_1) = 0, \qquad (1.6)$$

where $\varphi_{N0}(r_2) = r_2\phi_{N0}(r_2)$ and $u_N^{\mathrm{H}}(r_1) = r_1 U_N^{\mathrm{H}}(r_1)$.

In the next section we shall first approximate $V_N^{\mathrm{H}}(r)$ such that the resultant scattering equation can be analytically solved. We shall derive analytical expressions for the amplitude and the phase shifts, specifically their dependence on N and E. From the analytical expressions, as a function of N, we can analytically continue the final state wave function and deduce the energy dependence of the matrix element. Finally, from the matrix element we can derive the ionization threshold law. For the approximate potential the result is characterized by an exponentially damped energy dependence, which has a qualitative similarity to the result of Macek and Ihra [4]. We also consider the Hartree potential itself. This can only be done numerically, and has required considerable developments in order to deal with states of high N. Comparison shows that the numerical solution *for the amplitude* is essentially identical to the analytical result of our approximation of the Hartree potential. The Hartree phase shifts are only slightly increased. But this increase, which only depends on the total energy, does not affect the analytic continuation, and therefore the threshold law. It is therefore concluded that the optical potential appropriate to the TP model must also be included in order to make a direct comparison with the Macek and Ihra result. The section concludes with a quantum mechanical interpretation of the result, and the outlook of this approach for the complete $(2/r_{12})$ problem.

II. APPROXIMATION TO THE HARTREE POTENTIAL

The Hartree potential $V_N^{\mathrm{H}}(r)$ of Eq. (1.5) can be approximated for large N by expanding the integral in powers of $1/N$, retaining the lowest-order terms. We obtain

$$W_N(r) = \begin{cases} -2/r + 2/N^2, & r \leqslant r_c = N^2 \\ 0, & r \geqslant r_c = N^2 \end{cases}. \tag{2.1}$$

In Fig. 1, we show $W_N(r)$ and $V_N^{\mathrm{H}}(r)$ for several values of N. The difference between the Hartree potential and the approximate potential, $W_N(r) - V_N^{\mathrm{H}}(r)$, is greatest at $r = r_c$.

A. Analytical solution

The main advantage of using $W_N(r)$ is that it allows an analytic solution of the scattering equation,

$$\left[-\frac{d^2}{dr_1^2} + W_N(r_1) - k_N^2\right] u_N^W(r_1) = 0. \tag{2.2}$$

Specifically in the region $r \leqslant r_c$, the equation for $u_N^W(r)$ can be written as

$$\left[-\frac{d^2}{dr^2} - \frac{2}{r} - q_N^2\right] u_N^W(r) = 0, \tag{2.3}$$

where

$$q_N^2 = E - \frac{1}{N^2}. \tag{2.4}$$

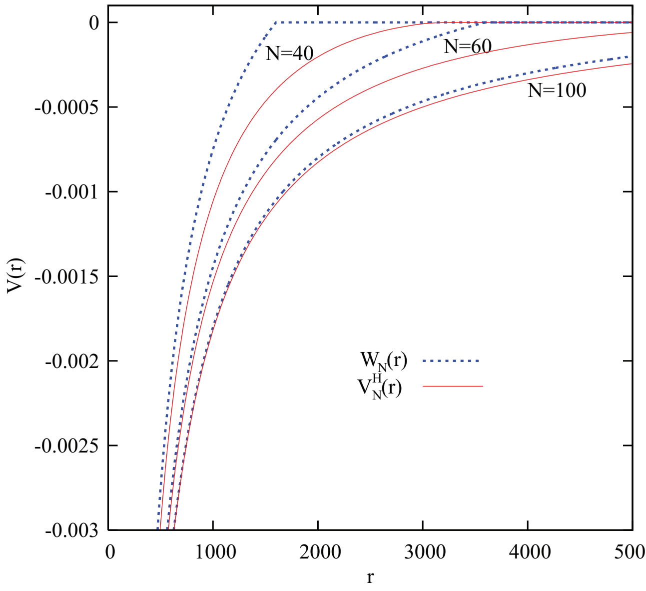

FIG. 1. (Color online) The Hartree potential $V_N^{\mathrm{H}}(r)$ and the approximate potential $W_N(R)$ are compared for several values of N (in Rydberg units).

The solution of (2.3) is the well-known Coulomb wave function

$$u_N^W(r < r_c) = r \exp(-iq_N r) F_{ch}(1 + i/q_N;\, 2;\, 2iq_N r). \tag{2.5}$$

$F_{ch}(a;\, b;\, c)$ is a confluent hypergeometric function [5]; (in Ref. [5] this function is called $M(a,b,c)$.) The function $u_N^W(r)$ is such that its asymptotic form, assuming $q_N r \gg 1$ (even though $r \leqslant r_c$) approaches [5]:

$$u_N^W(r < r_c) \cong \frac{1}{C_0(q_N)} \sin[\theta_0(q_N, r)], \tag{2.6}$$

where

$$\theta_0(q_N, r) = q_N r + \frac{\ln(2q_N r)}{q_N} + \arg\Gamma\left(1 - \frac{i}{q_N}\right), \tag{2.7}$$

and

$$C_0(q_N) = \sqrt{\frac{2\pi\, q_N}{[1 - \exp(-2\pi/q_N)]}}. \tag{2.8}$$

(Our $C_0(q)$ is $qC_0(-1/q)$ of Ref. [5].) When q_N is small, $C_0 \approx \sqrt{2\pi q_N}$ and the last term of (2.7) can be evaluated to high accuracy from [5]

$$\arg\Gamma\left(1 - \frac{i}{q_N}\right) \approx \frac{\ln(q_N)}{q_N} + \frac{1}{q_N} - \frac{\pi}{4}. \tag{2.9}$$

The phase shifts and the amplitudes are determined, in the usual way, by equating the solution and its derivative to the plane s wave [which is the solution of (2.2) for $r \geqslant r_c$] at $r = r_c$. For $r \geqslant r_c$ the solution is normalized as [6]

$$u_N^W(r > r_c) = \frac{A_N^W}{k_N} \exp\left(i\eta_N^W\right) \sin\left(k_N r + \eta_N^W\right). \tag{2.10}$$

Ordinarily the presence of the phase factor is not important in determining the scattering parameters, but in our application, as a result of the analytic continuation, its presence is crucial. Equating the logarithmic derivative, the absolute phase shift [7] (in the limit of large N) is given by

$$\eta_N^W = -\frac{1}{\sqrt{E}} + \frac{\ln\left(2q_N^2 N^2\right)}{q_N} + \frac{1}{q_N} - \frac{\pi}{4}, \tag{2.11}$$

and the amplitude is

$$A_N^W = \frac{E^{1/4}}{\sqrt{2\pi}} \equiv A_E. \tag{2.12}$$

Note A_N^W is independent of N and depends only on E (and, as we shall see, this also holds in the Hartree case). [In calculating the matrix element, one must divide by A_E; see Sec. V below.]

B. Numerical solution

We obtained the absolute phase shift η_N^W and the amplitude A_N^W for the approximate potential $W_N(r)$ by two independent numerical methods. First, we applied the Calogero method [8]. In this approach, one solves the differential equation

$$\frac{d\eta_N^W(r)}{dr} = -\frac{W_N(r)}{k_N} \sin^2\left[k_N r + \eta_N^W(r)\right], \tag{2.13}$$

with the initial condition $\eta_N^W(0) = 0$. The absolute phase is given by $\eta_N^W \equiv \eta_N^W(r_c)$, since $W_N(r) = 0$ for $r > r_c$. We used

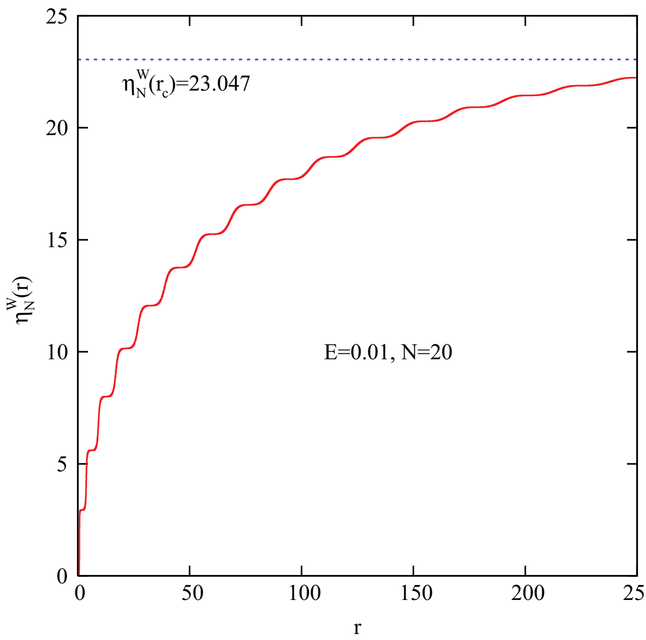

FIG. 2. (Color online) The evolution of $\eta_N^W(r)$ for $N = 20$ and $E = 0.01$ from the Calogero method (in Rydberg units).

a finite difference approximation, with 50 000 000 iterations in order to obtain the desired convergence for $10 \leqslant N \leqslant 200$. The corresponding amplitude is given by

$$A_N^W(r) = \int_0^r \frac{W_N(r')}{2k_N} \sin\left[2k_N r' + 2\eta_N^W(r')\right] dr'. \tag{2.14}$$

Similarly, $A_N^W \equiv A_N^W(r_c)$. In Fig. 2, we show $\eta_N^W(r)$ for $N = 20$ and $E = 0.01$. Note that the function approaches its final value in a steplike fashion.

We also obtained values for the phase shift and amplitude using a completely independent method. We directly solved Eq. (2.2) using the finite element method (FEM) [9]. We imposed the asymptotic boundary condition at $r = r_c$,

$$\tilde{u}_N^W(r_c) = \frac{1}{k_N}\left[\sin(k_N r_c) + \tan\delta_N^W \cos(k_N r_c)\right], \tag{2.15}$$

and

$$\frac{d\tilde{u}_N^W}{dr} = \cos(k_N r_c) - \tan\delta_N^W \sin(k_N r_c), \tag{2.16}$$

where δ_N^W is the phase shift (modulo 2π) and $\tilde{u}_N^W(r)$ is related to $u_N^W(r)$ by

$$u_N^W(r) = A_N^W \cos\delta_N^W\, \tilde{u}_N^W(r). \tag{2.17}$$

The solution of the FEM equations yields a piecewise continuous function $\tilde{u}_N^W(r)$ and the phase shift δ_N^W. We confirm the accuracy of δ_N^W and obtain the normalization factor A_N^W by using the integral formulas

$$\tan\delta_N^W = -\int \sin(k_N r) W_N(r) \tilde{u}_N^W(r) dr, \tag{2.18}$$

$$\left[A_N^W\right]^{-1} = \cos(\delta_N^W)\left[1 - \int \cos(k_N r) W_N(r) \tilde{u}_N^W(r) dr\right]. \tag{2.19}$$

(These equations are derived in Appendix A.)

TABLE I. Absolute phase shifts η_N^W and amplitudes A_N^W for the W_N potential obtained using the Calogero method and by a direct solution of the differential equation. Also included (for $N = 200$) are the large N analytical results from Eqs. (2.11) and (2.12).

	$E = 0.01$		$E = 0.02$		$E = 0.05$	
N	η_N^W	A_N^W	η_N^W	A_N^W	η_N^W	A_N^W
20	23.047	0.1333	20.154	0.1545	16.156	0.1910
40	35.006	0.1281	29.103	0.1512	22.073	0.1892
60	42.594	0.1270	34.164	0.1505	25.630	0.1889
80	48.126	0.1266	38.591	0.1503	28.175	0.1888
100	52.473	0.1265	41.699	0.1502	30.157	0.1887
120	56.050	0.1264	44.249	0.1502	31.779	0.1887
140	59.088	0.1263	46.411	0.1501	33.153	0.1887
160	61.728	0.1263	48.287	0.1501	34.343	0.1887
180	64.062	0.1263	49.944	0.1501	35.394	0.1887
200	66.153	0.1262	51.428	0.1501	36.335	0.1887
200[a]	66.132	0.1262	51.411	0.1500	36.315	0.1886

[a] Analytical results from Eqs. (2.11) and (2.12).

In order to obtain the absolute phase, we use

$$\eta_N^W = \delta_N^W + n\frac{\pi}{2}, \tag{2.20}$$

where n is the number of extra nodes in $\tilde{u}_N^W(r)$ relative to $\sin(k_N r)$.

Results are given in Table I; the phase shifts and the amplitude obtained by two independent numerical methods agreed to at least the number of digits reported. We also include the results obtained with the analytic (large N) formulas (2.11) and (2.12) at $N = 200$. In Fig. 3 we plot the phase

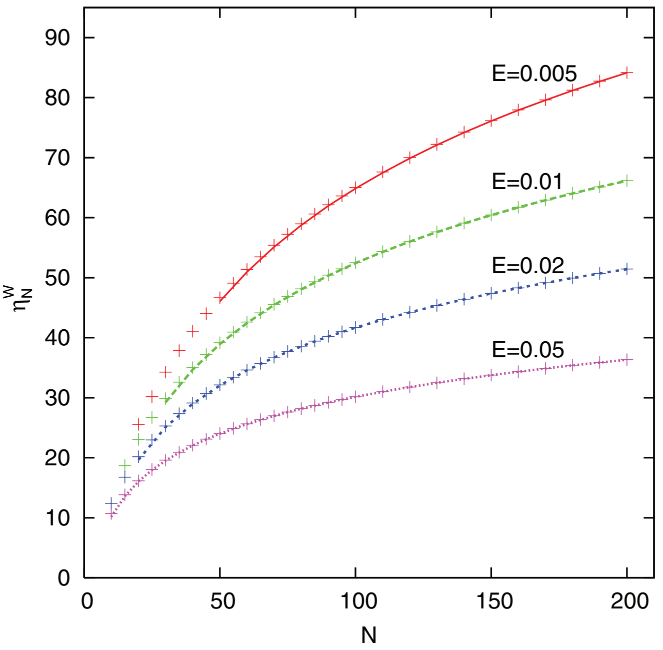

FIG. 3. (Color online) The absolute phase shift η_N^W for the approximate potential W_N at four energies (in Rydberg units). The crosses are the numerical results and the lines are the large N analytical results from Eq. (2.11).

TABLE II. Numerical results for the absolute phase shifts η_N^{H} and amplitudes A_N^{H} for the Hartree potential.

	$E = 0.01$		$E = 0.02$		$E = 0.05$	
N	η_N^W	A_N^W	η_N^W	A_N^W	η_N^W	A_N^W
			13.880	0.1660	11.815	0.1974
20	25.472	0.1334	22.039	0.1545	17.439	0.1910
30	32.546	0.1295	27.311	0.1521	20.911	0.1897
40	37.837	0.1281	31.177	0.1512	23.418	0.1892
50	42.049	0.1274	34.225	0.1508	25.379	0.1890
60	45.541	0.1270	36.737	0.1505	26.990	0.1889
70	48.522	0.1268	38.874	0.1504	28.355	0.1888
80	51.121	0.1266	40.733	0.1503	29.540	0.1888
90	53.424	0.1265	42.376	0.1503	30.587	0.1888
100	55.492	0.1265	43.850	0.1502	31.524	0.1888

shift at four energies, and compare with the large N analytic results.

III. HARTREE POTENTIAL

For the approximate potential W_N, one can obtain an analytical solution of the scattering equation in the large N limit. For the Hartree potential, given by Eq. (1.5), one must employ the numerical techniques that were described in Sec. II B. Indeed it has proven to be a difficult numerical task to evaluate $V_N^{\mathrm{H}}(r)$ for large N; we discuss the techniques that were developed to obtain accurate values of the Hartree potential in Appendix B. For $N < 100$, the results from the Calogero method and the FEM agreed to within the accuracy reported in Table II. The Calogero method became computationally prohibitive for large N, as the Hartree potential had to be evaluated at each iteration. For $N > 100$, we used the FEM to obtain the phase shifts and amplitudes.

The amplitude for the Hartree potential $V_N^{\mathrm{H}}(r)$ is the same as for the approximate potential $W_N(r)$ at all values of N and E. This means the amplitude is essentially determined by the small r behavior of the potential, where $V_N^{\mathrm{H}}(r) \approx W_N(r)$. The absolute phase shifts, however, are different. In Fig. 4 we plot the absolute phase shift as a function of N. Comparing Fig. 4 with Fig. 3, it is obvious that the *shape* of the four curves is essentially unchanged, although the magnitude is shifted upward. For large N, the absolute phase shift for the Hartree potential was fit (with a high degree of accuracy) to

$$\eta_N^{\mathrm{H}} = \eta_N^W + \frac{0.30}{\sqrt{E}}. \tag{3.1}$$

IV. ANALYTIC CONTINUATION

We now consider the analytic continuation of the scattering parameters corresponding to the inner electron going from an excited s state, $\varphi_N(r)$, into the continuum, $\varphi_\varepsilon(r)$. The analytic continuation is deduced by comparing the respective wave functions, which are normalized as $\varphi(r \to 0) \to r$. The bound state is

$$\varphi_N(r) \equiv r\phi_N(r) \propto r\exp(-r/N)F_{ch}(1-N;\,2;\,2r/N), \tag{4.1}$$

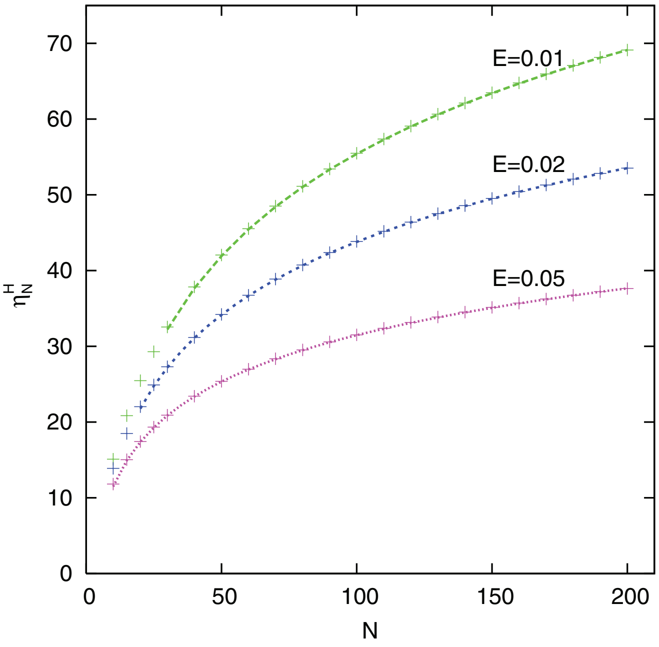

FIG. 4. (Color online) The absolute phase shift η_N^{H} for the Hartree potential at three energies (in Rydberg units). The crosses are the numerical results and the lines are the analytical fit given by Eq. (3.1).

and the continuum state is

$$\varphi_\varepsilon(r) \propto r\exp(-i\sqrt{\varepsilon}r)F_{ch}(1+i/\sqrt{\varepsilon};\,2;\,2ir\sqrt{\varepsilon}), \tag{4.2}$$

where, to repeat, $F_{ch}(a;\,b;\,c)$ is the confluent hypergeometric function. The quantity ε is the final (positive) energy of the inner electron after it has escaped from the nucleus. Comparing, we see that Eq. (4.1) goes into Eq. (4.2) when

$$N \to -\frac{i}{\sqrt{\varepsilon}}. \tag{4.3}$$

Equation (4.3) defines the analytic continuation. (This analytic continuation applies only to the function $\varphi_N(r)$; the outer electron is a continuum wave in all cases.) The analytical continuation $\varphi_N \to \varphi_\varepsilon$ is well known, but it is not trivial; it involves continuing a real integer N into the inverse of an imaginary momentum $i\sqrt{\varepsilon}$. Physically this represents the transition of bound (i.e., cyclic) motion into (in this case) an outgoing radial (i.e., noncyclic) motion As we shall see, this has profound mathematical consequences for the threshold law.

Note first that N^2 becomes negative:

$$N^2 \to -1/\varepsilon, \tag{4.4}$$

so that the formulas for k_N^2 and q_N^2 become

$$k_N^2 \to k_\varepsilon^2 = E - \varepsilon, \tag{4.5}$$

$$q_N^2 \to q_\varepsilon^2 = E + \varepsilon. \tag{4.6}$$

Thus from (2.11), the phase shift for $V_N^W(r)$ goes into

$$\eta_\varepsilon^W \to -\frac{1}{\sqrt{E}} + \frac{\ln\left(-2q_\varepsilon^2/\varepsilon\right)}{q_\varepsilon} + \frac{1}{q_\varepsilon} - \frac{\pi}{4}. \tag{4.7}$$

The branch cut in the scattering plane is along the positive momentum axis, implying that -1 in the logarithm must be interpreted as $-1 = e^{i\pi}$.

Hence we see that the phase shift has become complex with real and imaginary parts given by

$$\mathrm{Re}\big[\eta_\varepsilon^W\big] = -\frac{1}{\sqrt{E}} + \frac{\ln\big(2q_\varepsilon^2/\varepsilon\big)}{q_\varepsilon} + \frac{1}{q_\varepsilon} - \frac{\pi}{4} \tag{4.8}$$

and

$$\mathrm{Im}\big[\eta_\varepsilon^W\big] = \frac{\pi}{q_\varepsilon}. \tag{4.9}$$

For the Hartree potential, from Eq. (2.20), we see that only the real part has been augmented:

$$\mathrm{Re}\big[\eta_\varepsilon^{\mathrm{H}}\big] = \mathrm{Re}\big[\eta_\varepsilon^{\mathrm{W}}\big] + \frac{0.30}{\sqrt{E}}, \tag{4.10}$$

while the imaginary part is not affected:

$$\mathrm{Im}\big[\eta_\varepsilon^{\mathrm{H}}\big] = \mathrm{Im}\big[\eta_\varepsilon^W\big] = \frac{\pi}{q_\varepsilon}. \tag{4.11}$$

V. THE THRESHOLD LAW

The threshold law for ionization is by definition the yield of positive ions resulting from the collision, as an analytical function of the available energy E, in the limit $E \to 0$. The general formula for the yield, which is derived from Fermi's "golden rule" [10], integrated over all ionization states of total energy E, which in our case contains no angles, can be reduced to

$$Q(E) \propto \iint |\mathrm{ME}|^2 \delta\big(E - k_\varepsilon^2 - \varepsilon\big) k_\varepsilon d\, k_\varepsilon^2 \sqrt{\varepsilon}\, d\varepsilon. \tag{5.1}$$

ME is the transition matrix element. The integration over k_ε^2 can be carried out directly giving

$$Q(E) \propto \int |\mathrm{ME}|^2 \sqrt{E-\varepsilon}\sqrt{\varepsilon} d\varepsilon. \tag{5.2}$$

At this point it is convenient to consider the reaction as photo–double detachment (PDD) of H$^-$ rather than electron-impact ionization of H, so that the matrix element in the TP model is proportional to

$$\mathrm{ME} \propto \langle \Psi_f(r_1,r_2) | (r_1 + r_2) | \Phi_i(r_1,r_2) \rangle. \tag{5.3}$$

[Since Φ_i and $(r_1 + r_2)$ are symmetric in $(r_1 \leftrightarrow r_2)$, it is not necessary for $\Psi_f(r_1,r_2)$ to be symmetric; however, it is understood that we are dealing with the singlet case, although the exchange terms in *PHP* in Eq. (1.1) have here been omitted, because they are negligible for large N.] The advantage of the PDD matrix element is that there is no question that the exact initial bound state of H$^-$ ion, $\Phi_i(r_1,r_2)$, is independent of the final state energy E, and that the integral is convergent. (In the TP model H$^-$ continues to be bound with about half its full electron affinity [11].)

On the other hand, the final state does depend on E; it can be written (after the analytic continuation has been made) as

$$\Psi_f(r_1,r_2) = \frac{e^{i\eta_\varepsilon}}{A_E} \frac{u_k(r_1)}{r_1} \frac{\varphi_\varepsilon(r_2)}{r_2}, \tag{5.4}$$

where $\Psi_f(r_1,r_2)$ has the correct asymptotic form required in the ME. For the scattered (outer) electron, i.e., the solution of Eq. (2.2),

$$\frac{e^{i\eta_\varepsilon}}{A_E} u_k(r_1) \to e^{i\eta_\varepsilon} \frac{\sin(kr_1 + \eta_\varepsilon)}{k}. \tag{5.5}$$

The function $\varphi_\varepsilon(r_2)$, which represents the inner electron, has the asymptotic form

$$\varphi_\varepsilon(r_2 \to \infty) = \frac{\sin[\theta_0(\sqrt{\varepsilon},r_2)]}{\sqrt{\varepsilon}}. \tag{5.6}$$

The exact form of $\varphi_\varepsilon(r_2)$ with the above normalization is [5]

$$\varphi_\varepsilon(r_2) = \frac{\sqrt{2\pi}}{\varepsilon^{1/4}} r_2 \exp(-ir_2\sqrt{\varepsilon}) F_{ch}(1 + i/\sqrt{\varepsilon}; 2; 2ir_2\sqrt{\varepsilon}). \tag{5.7}$$

The initial state, $\Phi_i(r_1,r_2)$, vanishes exponentially when either r_1 or r_2 is large. Near the origin, which is the essential part of the function that contributes to the matrix element (ME), the function $\varphi_\varepsilon(r_2)$ reduces to

$$\varphi_\varepsilon(r_2 \to 0) = \frac{\sqrt{\pi}}{\varepsilon^{1/4}} \sqrt{r_2}\; J_1(\sqrt{8r_2}), \tag{5.8}$$

where $J_1(x)$ is the Bessel function of order 1. But $u_k(r_1)$ in Eq. (5.4) is also dominated by its Coulomb ($-2/r_1$) potential near the origin, so that

$$u_k(r_1 \to 0) = \frac{1}{\sqrt{2}} \sqrt{r_1} J_1(\sqrt{8r_1}). \tag{5.9}$$

In toto, the part of Ψ_f that contributes to the matrix element is

$$\Psi_f \propto \frac{e^{i\eta_\varepsilon}}{A_E \varepsilon_{1/4}} \frac{1}{\sqrt{r_1 r_2}} J_1(\sqrt{8r_1})\; J_1(\sqrt{8r_2}), \tag{5.10}$$

and the matrix element, in explicit form, reduces to

$$\begin{aligned} \mathrm{ME} \propto \frac{e^{i\eta_\varepsilon}}{\varepsilon^{1/4} A_E} \iint & J_1(\sqrt{8r_1}) J_1(\sqrt{8r_2})(r_1 + r_2) \\ & \times \Phi_i(r_1,r_2) r_1^{3/2} r_2^{3/2} dr_1 dr_2. \end{aligned} \tag{5.11}$$

The integral in (5.11) is manifestly independent of E, thus the ME is proportional to

$$\mathrm{ME} \propto \frac{e^{i\eta_\varepsilon}}{\varepsilon^{1/4} A_E}. \tag{5.12}$$

Now, using (2.12) for A_E, and inserting ME into the yield formula (5.2) (recall $\varepsilon \leqslant k_\varepsilon^2 \Rightarrow \varepsilon_{\max} = E/2$), we are left with

$$\begin{aligned} Q(E) &\propto \frac{1}{E^{1/2}} \int_0^{E/2} e^{i\eta_\varepsilon - i\eta_\varepsilon^*} \sqrt{E-\varepsilon}\, d\varepsilon \\ &= \frac{1}{E^{1/2}} \int_0^{E/2} e^{-2\mathrm{Im}[\eta_\varepsilon]} \sqrt{E-\varepsilon}\, d\varepsilon. \end{aligned} \tag{5.13}$$

Here we see the significance of the imaginary part of the phase shift. It is crucial to know the dependence of η_ε on ε and E. For the potentials $W_N(r)$ and $V_N^{\mathrm{H}}(r)$, η_ε is given by

Eq. (4.11) and q_ε is given by (4.6). As a result,

$$Q(E) \propto \frac{1}{E^{1/2}} \int_0^{E/2} e^{-2\pi/\sqrt{E+\varepsilon}} \sqrt{E-\varepsilon}\, d\varepsilon. \qquad (5.14)$$

One must integrate the above by parts to get the result in lowest order, which is the threshold law. The partial integration must be done carefully; without going into detail, we obtain

$$Q(E) \propto E^{3/2} e^{-\frac{\pi\sqrt{8/3}}{\sqrt{E}}} \cong E^{3/2} e^{-\frac{5.130}{\sqrt{E}}}. \qquad (5.15)$$

VI. DISCUSSION

Macek and Ihra [4] have obtained the threshold law (for the TP model):

$$Q_{MI}(E) \propto e^{-\frac{6.870}{(E/2)^{1/6}}}. \qquad (6.1)$$

[The original formula was given in atomic units, where $E(\text{a.u.}) = E(\text{Ry})/2$.] Their result has been supported by an analysis and calculation of Miyashita *et al.* [12] and a particularly cogent calculation of Bartlett and Stelbovics [13], using their version of the exterior complex scaling method of McCurdy and Rescigno [14]. In particular, when their numerical results near threshold were fitted to the form $\exp[-a(E/2)^{-b}]$ they determined as optimum parameters $a = 6.868 \pm 0.07$, $b = 0.169$. This is remarkable agreement with (6.1). Therefore, pending the inclusion of the optical potential (see below), we believe the Macek-Ihra result is essentially correct.

We shall try to understand these results quantum mechanically, and again we find it preferable to think of the process as two-electron photodetachment (i.e., photo–double detachment) of H^-. To photo–double detach both electrons from H^- requires a photon energy of ~14.0 eV (in the TP model, the second electron is bound by ~0.37 eV = 0.027 Ry [11].) This corresponds to a photon of wavelength $\lambda \sim 1500 a_0$. Spatially, that is more than sufficient for the two outgoing electrons to absorb a single photon simultaneously. In the case of single photodetachment plus *excitation* of the inner electron, the inner electron is still in a *bound* orbit which means that it recycles and therefore has much more *time* (i.e., a greater probability) of simultaneously absorbing the photon with the scattered electron. In photo–double detachment, the inner electron is in an escaping orbit, so it does not recycle and therefore, the inner electron has only one chance of being absorbed simultaneously with the outer (scattered) electron. Thus the probability of double escape (near threshold) is drastically reduced relative to single detachment plus excitation. This implies that the cross section for single photodetachment plus excitation (to the Nth) level is *not* a smooth function of N as N goes into the continuum. Furthermore the faster the outer electron goes out, the less time there is for simultaneous absorption. In the W approximation there is no potential beyond $r > 1/\varepsilon$, so that the outer electron goes out too rapidly for the simultaneous absorption to take place. And, we see, the additional attraction present in the Hartree approximation is too small to affect that probability (to within a proportionality constant).

This leads to a discussion of the effect of the optical potential terms in the TP model. (Here, we go back to thinking in terms of the electron-hydrogen problem.)

Those terms correspond to the nonlocal potential [1] (above a given target state N),

$$P H_{\text{TP}} Q \frac{1}{E - Q H_{\text{TP}} Q} Q H_{\text{TP}} P \Psi\Big\rangle = \left(\sum_\nu + \int d\nu\right) \frac{P H_{\text{TP}} Q \Phi_\nu^N\rangle \langle \Phi_\nu^N Q H_{\text{TP}} P \Psi\rangle}{E - \varepsilon_\nu^N}, \qquad (6.2)$$

where the second term in the denominator,

$$\varepsilon_\nu^N = \langle \Phi_\nu^N Q H_{\text{TP}} Q \Phi_\nu^N \rangle, \qquad (6.3)$$

is an autoionization energy associated with the Nth state of the hydrogen target.

The right-hand side of (6.2) is an expansion of the optical potential in terms of the eigenfunctions and eigenvalues of $Q H_{\text{TP}} Q$, i.e., Φ_ν^N and ε_ν^N, all relative to the Nth threshold of the target hydrogen atom [1]. [As an aside, because of the orthogonality of P and Q, H_{TP} in (6.2) reduces to $H_{\text{TP}} \to 2/r_>(1,2)$**,** which is a positive definite potential.] In a related but different model, called the s-wave model, Meerwald *et al.* [15] have calculated eigenvalues up to $N = 7$, and found only one eigenvalue below each $(N+1)$ threshold of the target H atom. [The s-wave model replaces the spherical kinetic energy operator of the TP model, $\sum_i \frac{1}{r_i} \frac{\partial^2}{\partial r_i^2} r_i$, by a purely linear kinetic energy operator, $\sum_i \frac{\partial^2}{\partial x_i^2}$, where $-\infty < x_i < +\infty$, and the interaction is $-2/|x_1| - 2/|x_2| + 2/|x_>(1,2)|$.] Nevertheless it is not unreasonable to assume that a similar result holds for the TP model. (We know, in fact, that in the TP model [11] there is only one eigenvalue, ε_ν^N below the $N = 1$ state of hydrogen.) The significance of this is that the term in the optical potential associated with that eigenvalue is *repulsive* (i.e., since E is positive, the denominator of that term is positive, and the numerator is positive definite), whereas all the remaining terms are essentially *attractive* (of which there are in principle a continuous infinity of terms, but each of, presumably, increasingly smaller width as ν increases), because their denominators are *negative* (when E is close to threshold). The difference between our result and that of Macek and Ihra suggests the attractive effect will outweigh the repulsive term, but this is speculative, and the optical potential must obviously be calculated. (The calculation of the spectrum $\langle \Phi_\nu^N Q H_{\text{TP}} Q \Phi_\nu^N \rangle$ above arbitrary N states is in itself an interesting problem, which we have already started to explore.)

At this point one is tempted to contemplate the prospect of using this approach for the more realistic model wherein the e-e interaction $2/r_{12}$ is replaced by $2/(r_1 + r_2)$. This model, whose history is itself very interesting (cf. footnote 3 of [16]), has been subject to a multiplicity of names. In Ref. [13] it is called the "collinear model" and in Ref. [4] it is called the "linear model." Both these names are, in our opinion, inadequate, because the kinetic energy operator in this model Hamiltonian is the spherically symmetric part of the full kinetic energy, and the potential energy replaces $\cos\theta_{12} \to -1$ (meaning that the outgoing electrons are represented as shells, each attracted to the nucleus but repelling each other). We believe the name "spherically symmetric contralinear" (SSCL) more correctly describes the physics of the model. Explicitly, that Hamiltonian is thus

$$H_{\mathrm{SSCL}} = -\left(\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{(r_1+r_2)}. \tag{6.4}$$

We know that the autoionization spectrum of this model, as well as the full interaction $2/r_{12}$, gives an infinite number of eigenvalues below each $N \geqslant 2$ threshold of the target (hydrogen) [16,17]. Thus the phase shifts would approach infinity, so that the approach we have used here (for the W and Hartree approximations) would *not* be applicable.

But, continuing the discussion of the SSCL, note that it contains one of the main elements of the Wannier theory [18]: that the threshold is dominated by events in which the two emerging electrons are emitted on opposite sides of the nucleus ($\vec{r}_1 = -\vec{r}_2$), in which case $2/r_{12} \to 2/(r_1 + r_2)$. However, the SSCL does *not* necessarily contain the second basic assumption of the Wannier theory: that the magnitudes of the vectors are necessarily approximately equal ($r_1 \cong r_2$). In fact it has long been our contention that the *true* threshold is dominated by events for which $r_1 \geqslant 2r_2$ (and the reverse), from which one of us (A.T.) has derived a Coulomb-dipole threshold law [19]. This dichotomy, in our opinion, has still not been definitively resolved, although the best of recent numerical calculations [20] supports the Wannier assumption.

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APPENDIX A

Following the methods of Demkov [21], one can derive an integral expression for the s-wave phase shift δ (mod 2π); one can also obtain an integral expression for the amplitude A of the normalized reduced wave function. In both cases, the function in the integrand need not be normalized. The formulas presented below are completely general, for any finite range potential $V(r)$.

A function $u(r)$ which satisifies

$$\left[-\frac{d^2}{dr^2} + V(r) - k^2\right]u(r) = 0 \tag{A1}$$

is subject to the boundary conditions $u(r \to 0) = r$ and

$$\begin{aligned} u(r \to \infty) &= \frac{A}{k}\sin(kr+\delta) \\ &= \frac{A\cos\delta}{k}[\sin(kr) + \tan\delta\cos(kr)]. \end{aligned} \tag{A2}$$

The phase is defined in the appropriate quadrant so that A is positive. The function $\tilde{u}(r)$, which is also a solution of Eq. (A1), satisfies the asymptotic boundary condition

$$\tilde{u}(r \to \infty) = \frac{1}{k}[\sin(kr) + \tan\delta\cos(kr)]. \tag{A3}$$

The two functions are simply related by

$$u(r) = A\cos\delta\,\tilde{u}(r). \tag{A4}$$

For the free particle where $V(r) = 0$,

$$\left[-\frac{d^2}{dr^2} - k^2\right]\sin(kr) = 0, \tag{A5}$$

and equivalently,

$$\left[-\frac{d^2}{dr^2} - k^2\right]\cos(kr) = 0. \tag{A6}$$

To obtain an integral expression for the phase shift, Eq. (A1) is premultiplied by $\sin(kr)$ and Eq. (A5) is premultiplied by $u(r)$; integrating over r and subtracting the difference, one obtains

$$\begin{aligned} &\int \sin(kr)\left[-\frac{d^2}{dr^2} + V(r) - k^2\right]u(r)dr \\ &\quad - \int u(r)\left[-\frac{d^2}{dr^2} - k^2\right]\sin(kr)dr = 0. \end{aligned} \tag{A7}$$

The limits of integration are understood to be from 0 to ∞. Integrating by parts, and using the appropriate boundary conditions,

$$A\sin\delta = -\int \sin(kr)V(r)u(r)dr, \tag{A8}$$

or, equivalently, using Eq. (A4),

$$\tan\delta = -\int \sin(kr)V(r)\tilde{u}(r)dr. \tag{A9}$$

In order to obtain the integral formula for the amplitude A, Eq. (A1) is premultiplied by $\cos(kr)$ and Eq. (A6) is premultiplied by $u(r)$. Again, the equations are integrated over r and subtracted, yielding

$$\begin{aligned} &\int \cos(kr)\left[-\frac{d^2}{dr^2} + V(r) - k^2\right]u(r)dr \\ &\quad - \int u(r)\left[-\frac{d^2}{dr^2} - k^2\right]\cos(kr)dr = 0. \end{aligned} \tag{A10}$$

In this case, the integration by parts yields an additional contribution at $r = 0$,

$$[1 - A\cos\delta] = -\int \cos(kr)V(r)u(r). \tag{A11}$$

Again, using Eq. (A4), one can express the amplitude as an integral over the un-normalized function $\tilde{u}(r)$,

$$[A]^{-1} = \cos\delta\left[1 - \int \cos(kr)V(r)\tilde{u}(r)dr\right]. \tag{A12}$$

APPENDIX B

Here we show how to calculate the hydrogenic radial eigenfunctions numerically for arbitrary N, without loss of accuracy, in such a way as to allow the practical calculation of the Hartree potential.

The radial functions for the s states are

$$\varphi_N(r) = \frac{2}{N^{3/2}} r \exp(-r/N) F_{ch}(1-N;\,2;\,2r/N), \quad \text{(B1)}$$

where

$$F_{ch}(1-N;2;x) = \sum_{j=0}^{N-1} \frac{(N-1)!(-1)^j}{(N-1-j)!(j+1)!j!} x^j \quad \text{(B2)}$$

is the confluent hypergeometric function in terms of $x = 2r/N$. The evaluation of the function for large N using Eq. (B2) is problematic, because the coefficients of the polynomial alternate sign and vary in magnitude from 1 to $1/N!$. There is significant cancellation that leads to loss of accuracy when N is large. To circumvent this problem, we calculated the $N-1$ zeros, x_j^N, of $F_{ch}(1-N;2;x)$ using MAPLE with 50-digit precision. The root solver employed the Descartes rule of signs. In Eq. (1.5), we replaced the confluent hypergeometric function with a product of its zeros,

$$F_{ch}(1-N;\,2;\,x) = \prod_{j=1}^{N-1} \left(1 - \frac{x}{x_j^N}\right). \quad \text{(B3)}$$

The advantage to using the product representation is that there is no loss of accuracy in evaluating the function, although the zeros must be calculated to quadruple precision for large N. That is, there is no cancellation of significant digits as there would be from the summation representation, Eq. (B2). The Hartree potential becomes

$$V_N^H(r) = \int_{2r/N}^{\infty} \prod_{j=1}^{N} \exp(-x')\left(1 - \frac{x'}{x_j^N}\right)^2 \times \left(-\frac{1}{r} + \frac{2}{Nx'}\right) x'^2 dx'. \quad \text{(B4)}$$

The integral was evaluated numerically (using quadruple precision).

[1] A. Temkin, in *Atomic, Molecular, and Optical Physics Handbook*, edited by G. W. F. Drake (AIP, New York, 1996), p. 310.

[2] A. Temkin, Phys. Rev. **126**, 130 (1962).

[3] R. Poet, J. Phys. B **11**, 3081 (1978).

[4] J. H. Macek and W. Ihra, Phys. Rev. A **55**, 2024 (1997); J. H. Macek and S. Y. Ovchinnikov, *ibid.* **54**, 544 (1996).

[5] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, DC, 1964), Chap. 14.

[6] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1949), p. 105.

[7] A. Temkin, J. Math. Phys. **2**, 336 (1961).

[8] F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic Press, New York, 1967); The specific formula for the phase shift was first derived and used by P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

[9] K. Bathe and E. Wilson, *Numerical Methods of Finite Element Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1976).

[10] Kurt Gottfried, *Quantum Mechanics, Volume I: Fundamentals* (W. A. Benjamin, Inc., New York, 1966) p. 444.

[11] A. Temkin, A. K. Bhatia, and Y. S. Kim, J. Phys. B **19**, L701 (1986).

[12] N. Miyashita, D. Kato, and S. Watanabe, Phys. Rev. A **59**, 4385 (1999).

[13] P. I. Bartlett and A. T. Stelbovics, Phys. Rev. A **69**, 022703 (2004).

[14] C. W. McCurdy and T. N. Rescigno, Phys. Rev. A **62**, 032712 (2000).

[15] P. Meerwald, Ch. Eltschka, and H. Friedrich, Few-Body Syst. **29**, 157 (2000); H. Friederich, W. Ihra, and P. Meerwald, Aust. J. Phys. **52**, 323 (1999).

[16] A. Temkin and Y. Hahn, Phys. Rev. A **9**, 708 (1974).

[17] A. Temkin and J. F. Walker, Phys. Rev. **140**, A1520 (1965).

[18] G. H. Wannier, Phys. Rev. **90**, 817 (1953).

[19] A. Temkin, Phys. Rev. Lett. **49**, 365 (1982); M. K. Srivastava and A. Temkin, Phys. Rev. A **43**, 3570 (1991).

[20] P. L. Bartlett, A. T. Stelbovics, and I. Bray, Phys. Rev. A **68**, 030701 (2003).

[21] Y. N. Demkov, *Variational Principles in the Theory of Collisions* (Pergamon Press, New York, 1963).