

where F_2 is the generalized hypergeometric function in two variables.¹⁴

An approximation technique was given in I for

¹⁴ P. Appell and J. Kampé de Fériet, *Fonctions Hypergéométriques*, etc. (Gauthiers-Villars, Paris, 1926).

evaluating integrals containing many interelectron functions. For greatest accuracy, the technique depended upon the evaluation of integrals of the type, J_n . Equation A(2.4) thus allows this approximation technique to be used with the wave functions of this paper.

Variational Treatment of Electron-Hydrogen Atom Elastic Scattering

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The Hulthén-Kohn variational method is applied to the elastic scattering of electrons by hydrogen atoms. The trial function used is of a nonseparable form, allows for the virtual excitation of the 2s and 3s states, and contains a scaling parameter which is allowed to vary. The resulting scattering lengths and S , P , and D singlet and triplet phase shifts are compared with the results of other calculations, and reasons are given for expecting them to be of improved accuracy.

I. INTRODUCTION

THE elastic scattering of electrons by hydrogen atoms is the simplest example of atomic scattering involving a composite system. As such it is not tractable by exact analytic means, and has been the subject of numerous successively improved calculations involving various approximation techniques. As there have recently appeared several papers¹ containing excellent reviews of the subject, we will not attempt to include one here. This paper is concerned with a Hulthén-Kohn variational calculation for the S , P , and D phase shifts, making use of a more flexible trial function than has so far been used. It is expected that this will substantially improve the existing values in a manner similar to the rapid improvement of the bound-state energy of a two-electron system when more elaborate trial functions are used in the Ritz variational procedure.

II. HULTHÉN-KOHN VARIATIONAL METHOD

In the atomic units in which length is expressed in Bohr radii and energy in double rydbergs, the Hamiltonian for the electron-hydrogen atom system is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}. \quad (1)$$

The asymptotic boundary condition for a given trial partial wave function satisfying the Schrödinger equation,

$$(H - E)\Psi = 0, \quad (2)$$

may be expressed as

$$\Psi_t \underset{r_1 \rightarrow \infty}{\sim} \psi_0(r_2) Y_{10}(\hat{\mathbf{r}}_1) r_1^{-1} \times \begin{cases} b_t \sin(kr_1 - \frac{1}{2}l\pi) + a_t \cos(kr_1 - \frac{1}{2}l\pi) \\ \text{or} \\ \alpha \sin(kr_1 + \eta_t - \frac{1}{2}l\pi), \end{cases} \quad (3)$$

where $\psi_0(r)$ is the ground-state hydrogen wave function $e^{-r}/\sqrt{\pi}$, and $Y_{10}(\hat{\mathbf{r}}_1)$ is the normalized Legendre polynomial $[(2l+1)/4\pi]^{\frac{1}{2}} P_l(\cos\theta_1)$; $\hat{\mathbf{r}} \equiv \mathbf{r}/r$. In addition to the above asymptotic condition, the trial function must (1) be symmetric or antisymmetric in \mathbf{r}_1 and \mathbf{r}_2 , (2) satisfy the boundary conditions at the origin of \mathbf{r}_1 and \mathbf{r}_2 , and (3) be an eigenfunction of the z component and square of the total angular momentum.

Consider the integral

$$L_t = \iint \Psi_t (H - E) \Psi_t d\tau_1 d\tau_2, \quad (4)$$

in which Ψ_t satisfies all the preceding conditions and contains the additional variational parameters c_1, c_2, \dots, c_n . The Hulthén-Kohn stationary expression is

$$\delta L_t = \alpha^2 k \delta \eta_t = k [b_t \delta a_t - a_t \delta b_t]. \quad (5)$$

The variation in L_t is performed with respect to all other parameters that may be contained by Ψ_t as well as the asymptotic parameters, η_t, a_t , and b_t . As we may choose the asymptotic amplitude to be $\alpha = 1$, the two phase parameters a_t and b_t cannot be varied independently. Choosing $a_t = 1$ and $\delta a_t = 0$ leads to the second Hulthén method² (called this to differentiate from the original Hulthén method), with the condition

$$\delta L_t = -k \delta b_t, \quad (6)$$

¹ H. S. W. Massey, *Revs. Modern Phys.* **28**, 199 (1956); B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, *Proc. Phys. Soc. (London)* **71**, 877 (1958); F. B. Malik, *Z. Naturforsch.* **14a**, 172 (1959).

² L. Hulthén, *Arkiv Mat. Astron. Fysik* **35A**, No. 25 (1948).

which requires that the variational parameters are determined by

$$\partial L_i / \partial c_i = 0 \quad (i=1, 2, \dots, n), \quad \partial L_i / \partial b_i = -k. \quad (7)$$

The resulting second-order phase parameter and phase shift are

$$b = b_i + L_i/k, \quad (8)$$

and

$$\eta = \operatorname{arccot} b. \quad (9)$$

Similarly, if we choose $b_i = 1$ and $\delta b_i = 0$, the corresponding relations of the Kohn³ method follow:

$$\delta L_i = k \delta a_i, \quad (10)$$

$$\partial L_i / \partial c_i = 0 \quad (i=1, 2, \dots, n), \quad \partial L_i / \partial a_i = k, \quad (11)$$

$$a = a_i - L_i/k, \quad (12)$$

$$\eta = \arctan a. \quad (13)$$

The two schemes are linearly independent and become identically equivalent only if $L_i = 0$. The original Hulthén method⁴ does not treat the asymptotic phase parameter as a variational parameter, and hence $\delta L_i = 0$. As this leads to only n equations in $n+1$ unknowns (c_i 's and a_i), the subsidiary condition $L_i = 0$ is also invoked.

The connection between the three methods was clearly demonstrated in a paper by Demkov and Shepelenko.⁵ If the c_i 's enter the trial function linearly one obtains from (5) a set of $n+2$ linear homogeneous equations in the c_i 's, a_i , and b_i . The first two equations contain a_i , b_i , and the c_i 's, while the last n equations contain only the c_i 's. As the determinant of the coefficients does not in general vanish, a nontrivial solution for the $n+2$ unknowns does not exist. In the second Hulthén and Kohn methods, the $n+2$ homogeneous equations are converted to $n+1$ nonhomogeneous equations in $n+1$ unknowns, which can be nontrivially solved, by setting $a_i = 1$, $\delta a_i = 0$, or $b_i = 1$, $\delta b_i = 0$, respectively. The original Hulthén method is equivalent to retaining the last n equations ($\delta L_i = 0$) and replacing the first two linear equations by the quadratic equation in a_i and c_i 's corresponding to $L_i = 0$. This has the effect of introducing a spurious nonphysical real root in addition to giving rise to the possibility of complex roots for a_i , both of which would then be nonphysical. Because of these ambiguities which may arise from the original Hulthén method and its greater numerical complexity we shall presently use only the Kohn and second Hulthén methods, which we shall refer to as Case A and Case B, respectively.

III. CHOICE OF TRIAL FUNCTION

In choosing a trial function we must make a compromise between desired accuracy and computational feasibility. It is desirable to choose a trial function which can be subsequently improved in a systematic way, giving results that will ultimately converge to the correct phase shifts.

We consider the form

$$\Psi_i(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\lambda=0}^{\infty} \{ Y_{10}(\hat{\mathbf{r}}_1) \Phi_{\lambda}(r_1, r_2) \pm Y_{10}(\hat{\mathbf{r}}_2) \Phi_{\lambda}(r_2, r_1) \} P_{\lambda}(\cos \theta). \quad (14)$$

Here θ is the angle between the two electron radius vectors. As shown by Breit,⁶ if the coordinates are transformed from $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$ to $r_1, \theta_1, \phi_1, r_2, \theta, \phi$, the transformed $\mathbf{L}^2 = (\mathbf{L}_1 + \mathbf{L}_2)^2$ operator does not contain any differential operators in θ . Hence, the above Ψ_i is an eigenfunction of \mathbf{L}^2 with eigenvalue $l(l+1)$. Also it is an eigenfunction of $L_z = L_{1z} + L_{2z}$ with eigenvalue $m=0$, since the transformed operator contains only $\partial/\partial \phi_1$.

Trial functions in the form of (14) have been used in Ritz variational calculations for the energy of bound states. Generally, the results were quite good even when only Φ_0 was retained and all higher Φ_{λ} 's omitted. For example, Chandrasekhar⁷ found a value for the total energy of the 1S state of H^- within 3% of its correct value with a trial function containing only the Φ_0 in (14). In a calculation on the $1s2p^3P$ state of He with a trial function in which $\Phi_1 = C\Phi_0$, Breit⁸ found that $C = -0.0089$ and the energy remains essentially unchanged from what it was with Φ_0 alone.

The Hylleraas type of trial function has been used even more extensively than (14) in energy calculations on two-electron systems. Green et al.⁹ have analyzed the 3 and 6 parameter Hylleraas function for the ground state of He in terms of a Legendre function expansion similar to (14). They found that the contribution to the total energy of the $\lambda=1, 2$, and 3 terms are approximately 0.01, 0.001, and 0.0002 of the $\lambda=0$ term. From this we see that the inclusion of the variable r_{12} in the trial function does not necessarily lead to an appreciable admixture of angular correlation terms.

These and other calculations¹⁰ indicate that an energy correct to within a few percent can be achieved with spherically symmetric trial functions if they have enough radial flexibility. This flexibility has been found to be greatly enhanced if the effective nuclear charge parameter is permitted to vary. We are thus encouraged

³ W. Kohn, Phys. Rev. **74**, 1763 (1948).

⁴ L. Hulthén, Kgl. Fysiograf. Sällskap. i Lund, Förh. **14**, No. 21 (1944).

⁵ Iu. N. Demkov and F. P. Shepelenko, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 1483 (1957) [translation: Soviet Phys.-JETP **33**, 1144 (1958)].

⁶ G. Breit, Phys. Rev. **35**, 569 (1930).

⁷ S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

⁸ G. Breit, Phys. Rev. **36**, 383 (1930).

⁹ L. C. Green, M. M. Mulder, P. C. Milner, M. N. Lewis, J. W. Woll, E. K. Kolchin, and D. Mace, Phys. Rev. **96**, 319 (1954).

¹⁰ See S. Chandrasekhar, Revs. Modern Phys. **16**, 301 (1944), and H. Bethe and E. E. Salpeter, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. XXXV, p. 204-256.

to expect phase parameters of comparable accuracy with a trial function of comparable flexibility, although our analogy between the energy and scattering calculations is only suggestive and certainly not rigorous.

Our present trial function for Case *A* is (14) with

$$\begin{aligned}\Phi_0(r_1, r_2) &= k\psi_0(r_2)[j_l(kr_1) - a_l(1 - e^{-r_1})^{2l+1}n_l(kr_1)] \\ &\quad + k[4\pi/(2l+1)]^{\frac{1}{2}}r_1^le^{-\gamma r_1}\sum_{n=1}^3 c_n R_{n0}(r_2), \quad (15) \\ \Phi_\lambda &= 0, \quad \lambda > 0,\end{aligned}$$

where j_l and n_l are the spherical Bessel and Neumann functions. For Case *B* we use the above form with $a_l = 1$ and b_l multiplying $j_l(kr_1)$. Here γ and the c_n 's are variational parameters and the R_{n0} 's are the unnormalized hydrogenic radial $1s$, $2s$, and $3s$ functions, e^{-r} , $e^{-r/2}(1-r/2)$, and $e^{-r/3}(1-2r/3+2r^2/27)$. The factors r_1^l and $(1-e^{-r_1})^{2l+1}$ are included to satisfy the boundary conditions at the origin. The scale parameter γ is analogous to the effective nuclear charge parameter in the energy calculations. As γ is always real and positive, the assumed trial function does not take explicit account of real excited states for $k^2 > 0.75$.

This trial function differs from the Hartree-Fock function in that it cannot be expressed as the product $F(r_1)\psi_0(r_2)$ (before symmetrization). The nonseparable terms belonging to $n=2$ and 3 in the above sum may be thought of as representing virtual excitations to the $2s$ and $3s$ states during the collision. Similarly the inclusion of terms for which $\lambda > 0$ would correspond to virtual excitations to p , d , \dots states, which would allow for a more complete description of the scattering. These virtual excitations also are included in the general term "polarization." As the adiabatic approximation is of questionable validity for this case,¹¹ we will consider polarization to exist only in the above sense of virtual excitations, rather than in terms of an added induced potential between the electron and the hydrogen atom.

IV. PROCEDURE OF CALCULATION AND RESULTS

The integrals contained in L_l have been incorporated into a general code for the IBM 704. They have been evaluated by a combination of analytical and numerical means for $l=0, 1$, and 2 . For any given value of γ , the resulting set of four linear equations, (7) or (11), in the parameters c_1 , c_2 , c_3 , and a_l (or b_l) is solved and the corresponding L_l is obtained.

As the c_n 's and a_l (or b_l) contained in L_l are functions of γ , for Case *A*

$$\frac{\partial L_l}{\partial \gamma} = \frac{dL_l}{d\gamma} - \sum_{n=1}^3 \frac{\partial L_l}{\partial c_n} \frac{dc_n}{d\gamma} - \frac{\partial L_l}{\partial a_l} \frac{da_l}{d\gamma} = -k \frac{da}{d\gamma},$$

and for Case *B*, $\partial L_l / \partial \gamma = kdb/d\gamma$. The points of zero

derivative of a and b with respect to γ thus correspond to the stationary condition $\partial L_l / \partial \gamma = 0$. For the *S* wave, most of the space integrals in L_l are considerably simpler than for $l > 0$ and can be evaluated completely analytically. An independent code was assembled for the *S* wave only to take advantage of this fact and was used as a check against numerical errors in the general code.

At each energy there may be any number of γ 's at which $\partial L_l / \partial \gamma = 0$, both for the Case *A* and Case *B* solutions. In general, the η 's corresponding to these different stationary points were very close to one another, in which case we chose for tabulation that stationary point whose γ value was most continuous with those of adjacent energies. When there existed a considerable spread in the η 's, the best one was assumed to correspond to the minimum absolute value of L_l , as the correct wave function would give $L_l = 0$. Since the trial functions used in Case *A* and Case *B* have different asymptotic normalizations, rather than compare the different values for L_l itself, we define the quantity

$$\begin{aligned}I &= L_l / (1 + a^2) \quad (\text{for Case } A) \\ &= L_l / (1 + b^2) \quad (\text{for Case } B),\end{aligned}$$

the minimum absolute value of which is our criterion for the preferred phase shift. The resulting phase shifts and variational parameters are given in Tables I, II, and III.

As a result of the inadequacy of our trial function for energies above the excitation threshold, we could in some cases not find a value of γ for which $\partial L_l / \partial \gamma = 0$ is satisfied. In these cases η tends to approach the same value asymptotically as γ gets very small or very large. We thus include the asymptotic η in the tables but omit the c_n parameters as they lose significance in the limit of $\gamma \rightarrow \infty$.

When η goes through 0 or $\pi/2$, b_l and b or a_l and a , respectively, go through a discontinuity, $\pm \infty$ to $\mp \infty$. Since this requires one of the unknowns (a_l or b_l) in the linear equations to become infinitely large in magnitude, the other terms containing the c_n 's become masked and errors are introduced. In those situations we use the method which results in a continuous change in the parameters, Case *A* when η goes through 0 and Case *B* when η goes through $\pi/2$. The phase shift has to be very close to 0 or $\pi/2$ for the above errors to enter, and it will be seen from the tables that with our coarse net in k the problem did not arise. For instance, Case *A* was used in both the singlet and triplet *S* wave for η 's near $\pi/2$.

The very low-energy behavior of the *S*-wave phase shifts can be expressed in terms of the scattering length, A_0 , and effective range, r_0 . These quantities are defined in the expansion of $k \cot \eta$ in powers of k^2 at zero energy,

$$k \cot \eta_0^\pm = -\frac{1}{A_0^\pm} + \frac{r_0^\pm}{2} k^2 + O(k^4). \quad (16)$$

We find $A_0^+ = 8.220$, $r_0^+ = 2.99$, $A_0^- = 2.350$, and r_0^-

¹¹ B. A. Lippmann, Bull. Am. Phys. Soc. **5**, 119 (1960); V. M. Martin, M. J. Seaton, and J. B. G. Wallace, Proc. Phys. Soc. (London) **72**, 701 (1958).

TABLE I. Variational parameters and phase shifts for S wave.

k	Case	γ	c_1	c_2	c_3	a_t (or b_t)	a (or b)	η
(Singlet)								
0.1	A	0.70	0.9288	-0.04832	0.003218	-1.024	-0.9373	2.389
0.2	A	0.93	1.070	-0.2378	0.3499	-3.116	-3.711	1.834
0.3	A	0.74	-2.790	0.03032	0.01236	10.92	12.19	1.489
0.4	B	0.86	-0.1819	-0.02140	-0.01484	0.2068	0.3879	1.201
0.6	B	0.75	-0.1247	0.001034	0.0000025	0.6998	0.8952	0.8406
0.8	A	0.78	-0.1369	-0.01681	-0.000487	0.9033	0.6640	0.5862
1.0	A	0.79	-0.07601	-0.005393	-0.001405	0.7257	0.5218	0.4809
1.5	A	0.82	-0.01476	0.000798	0.000294	0.8124	0.5028	0.4658
2.0	A	6.9	0.07939	-0.01103	-0.003166	1.380	0.5834	0.5281
(Triplet)								
0.2	A	0.66	0.1108	-0.006998	-0.001440	-0.5041	-0.4984	2.679
0.4	A	0.76	0.3631	-0.02015	-0.004194	-1.240	-1.220	2.257
0.6	A	1.04	-6.120	-0.01244	-0.000883	-2.891	-2.923	1.901
0.8	A	0.67	5.272	-0.4061	-0.05099	-20.74	-22.10	1.616
1.0	A	0.58	-2.527	0.3594	0.04783	4.601	6.849	1.426
1.5	A	0.62	0.01181	-0.004063	-0.000968	1.975	1.477	0.9756
2.0	A	0.82	-0.05346	0.001442	0.000206	1.406	1.000	0.7854

TABLE II. Variational parameters and phase shifts for P wave.

k	Case	γ	c_1	c_2	c_3	a_t (or b_t)	a (or b)	η
(Singlet)								
0.05	A	0.80	-0.005863	0.003536	-0.002500	0.0000532	0.0001960	0.000196
0.1	A	0.80	-0.01120	0.006617	-0.003978	0.0003740	0.0008170	0.000817
0.2	A	0.79	-0.01776	0.01013	-0.003059	0.001433	-0.002691	-0.002691
0.4	A	0.80	0.07830	0.01011	0.001337	-0.1070	-0.03952	-0.03950
0.6	A	0.77	0.006467	0.004347	0.001965	-0.07473	-0.09035	-0.09010
0.8	A	0.41	0.001308	-0.000420	0.000297	-0.07231	-0.1163	-0.1158
1.0	A	∞	-0.01646	-0.1043	-0.1040
1.5	A	∞	0.2371	0.009059	0.009059
2.0	A	∞	0.3851	0.1071	0.1066
(Triplet)								
0.05	A	0.79	0.007458	-0.004756	0.002179	0.0000479	0.0006958	0.000696
0.1	A	0.78	0.01395	-0.008864	0.003260	0.0004811	0.004794	0.004794
0.2	A	0.77	0.02590	-0.01491	0.001870	0.005135	0.02772	0.02771
0.4	B	0.88	-0.3385	-0.1834	-0.03489	6.971	7.037	0.1412
0.6	A	0.83	-0.01737	-0.02301	-0.006006	0.2811	0.2847	0.2774
0.8	A	0.72	-0.007277	-0.02202	-0.004456	0.3999	0.3791	0.3624
1.0	B	18	-0.02508	-0.003246	-0.001003	2.820	2.741	0.3498
1.5	B	∞	2.899	2.862	0.3361
2.0	B	∞	3.144	3.139	0.3084

TABLE III. Variational parameters and phase shifts for D wave.

k	Case	γ	c_1	c_2	c_3	a_t (or b_t)	a (or b)	η
(Singlet)								
0.2	A	0.83	-0.0002069	0.0002136	-0.0001004	0.000003684	-0.00005719	-0.000057
0.4	A	0.81	-0.0008756	0.0004411	-0.0000128	0.0001535	-0.001585	-0.001585
0.6	A	0.52	0.0003640	0.0000871	0.0000208	-0.002551	-0.007033	-0.007033
0.8	A	1.01	0.003939	0.0000173	0.0001909	-0.01286	-0.01404	-0.01404
1.0	A	∞	-0.004529	-0.01760	-0.01760
1.5	A	∞	0.03705	-0.001665	-0.001665
2.0	A	∞	0.1211	0.03330	0.03328
(Triplet)								
0.2	A	0.85	0.0004132	-0.0003690	0.0000886	0.00000584	0.0001655	0.000165
0.4	A	0.88	0.002106	-0.001189	-0.0000770	0.00007514	0.003420	0.003420
0.6	B	1.00	-0.3511	-0.1744	-0.03322	64.76	67.60	0.01479
0.8	A	0.87	-0.003364	-0.002754	-0.0005684	0.03323	0.03650	0.03649
1.0	B	∞	17.96	18.10	0.05520
1.5	B	∞	10.03	9.919	0.1005
2.0	B	∞	8.092	8.049	0.1236

TABLE IV. Variational and Born phases at higher energies.

k	η_0^+	η_0^-	η_0^{Born}	η_1^+	η_1^-	η_1^{Born}	η_2^+	η_2^-	η_2^{Born}
3.0	0.480	0.568	0.4903	0.1847	0.2673	0.2297	0.0887	0.1416	0.1160
4.0	0.442	0.483	0.4408	0.2087	0.2511	0.2322	0.1185	0.1496	0.1346
5.0	0.402	0.425	0.3993	0.2125	0.2368	0.2258	0.1320	0.1511	0.1419
6.0	0.368	0.382	0.3648	0.2084	0.2233	0.2164	0.1370	0.1494	0.1434

$= 1.22$ by extrapolating to zero energy the results of the variational calculation at very low energies ($k \approx 0.01$). The variational values for $k \cot \eta_0^\pm$ are plotted in Fig. 1. We cannot expect the linear relationship between $k \cot \eta$ and k^2 to hold for $k^2 \gtrsim 1/r_0^2$, which is seen to be the case in Fig. 1 $[(1/r_0^+)^2 = 0.113$ and $(1/r_0^-)^2 = 0.688]$.

We have also investigated the energy dependence of the P and D phase shifts for very low energies. The variational values of $\tan \eta_l$ were determined at $k = 0.01$, 0.015 , and 0.02 . The three values of $(\tan \eta_l)/k^{2l+1}$ plotted as a function of k^2 were found to fall on a straight line. Defining A_l^\pm as $\lim_{k \rightarrow 0} (-\tan \eta_l^\pm / k^{2l+1})$, we find the extrapolated values $A_1^+ = -1.904$, $A_1^- = -5.906$, $A_2^+ = 0.05175$, and $A_2^- = -0.7305$. In the adiabatic approximation where the asymptotic potential goes as $1/r^4$ it can be shown¹² that for $l > 0$, $\tan \eta_l \propto k^2$ as $k \rightarrow 0$. If this is the correct dependence it would imply that $\tan \eta_2^\pm / k^5$ should be a factor of 8 larger at $k = 0.01$ than it is at $k = 0.02$. Our results show this quantity changing by less than 5% between these two energies (with magnitude decreasing for the singlet and increasing for the triplet). It is unlikely that the variational phases could be in error by so large an amount, considering that there are 5 parameters in the trial function that are independently varied at each energy.

As previously mentioned our trial function is inadequate for $k^2 > 0.75$ because it does not include real excitation and ionization states. We did attempt to seek solutions for some large values of k with the result that we could not in all cases satisfy the condition $\partial L_l / \partial \gamma = 0$. However, the phases were not too sensitive to the choice of γ , and they tended to approach their Born approximation values

$$\eta_l^{\text{Born}} = \arctan \left[2k \int_0^\infty r^2 e^{-2r} \left(1 + \frac{1}{r} \right) j_l^2(kr) dr \right]. \quad (17)$$

Thus, keeping γ fixed at 1.5, we have determined the phases for higher energies by varying only the linear parameters. These results, expressed as the average of the Case A and Case B phase shifts, are given in Table IV together with the Born phases. Their estimated maximum uncertainty due to the averaging of the two cases is 0.01, 0.001, and 0.0001 radian for the S , P , and D waves, respectively.

The phase shifts can be used to calculate the various

total cross sections for electron scattering by hydrogen atoms, such as (in units of πa_0^2)

$$\sigma(\text{elastic}) = \frac{4}{k^2} \sum_{l=0}^{\infty} (2l+1) \left[\frac{1}{4} \sin^2 \eta_l^+ + \frac{3}{4} \sin^2 \eta_l^- \right],$$

$$\sigma(\text{momentum loss}) = \frac{4}{k^2} \sum_{l=0}^{\infty} (l+1) \left[\frac{1}{4} \sin^2(\eta_l^+ - \eta_{l+1}^+) + \frac{3}{4} \sin^2(\eta_l^- - \eta_{l+1}^-) \right],$$

$$\sigma(\text{spin exchange}) = \frac{1}{4k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\eta_l^+ - \eta_l^-),$$

and their corresponding differential values. The zero energy values of these total cross sections are $84.1\pi a_0^2$ (elastic and momentum loss) and $8.61\pi a_0^2$ (spin exchange).

V. CRITERIA FOR CORRECTNESS

Although the stationary expression for the phase shift resembles that for the ground-state energy in that the error is proportional to the square of the error in the trial function, the resulting phase shift at an arbitrary scattering energy is not a bound of any kind while the resulting ground-state energy is an upper bound to its correct value. This lack of a bound for the phase shift arises because the second order contribution to (8) or (12) cannot be shown in general to be either positive or negative. In the absence of such a rigorous bound, we

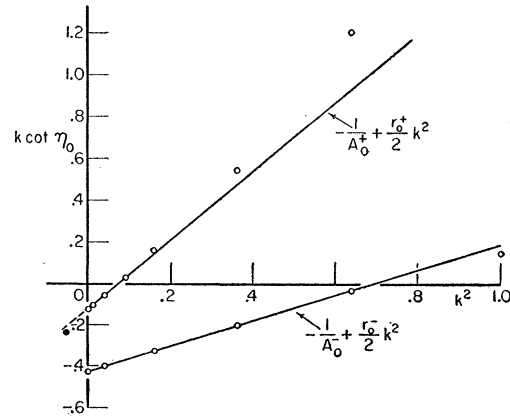


FIG. 1. Plot of $k \cot \eta_0$ versus k^2 . The upper set of open points correspond to the presently calculated singlet, and the lower set, triplet phase shifts. The limiting straight lines are also plotted together with the extension of singlet line to negative values of k^2 . The solid point is at $k \cot \eta_0^+ = -\alpha$, $k^2 = -\alpha^2$.

¹² B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958); hereinafter referred to as BDJS.

TABLE V. Variational parameters and $\tan\eta$ for Case A treatment of singlet S wave at $k=0.01$ as number of virtual states is increased.

γ	c_1	c_2	c_3	$\tan\eta$
0.71	0.6840	-0.08268
0.71	0.7537	-0.03003	...	-0.08232
0.71	0.7538	-0.03148	-0.001972	-0.08231
1.0	0.6660	-0.08680
1.0	0.3124	0.1886	...	-0.08596
1.0	0.01610	0.4954	-0.1637	-0.08445

can only infer the accuracy of our calculation from the sensitivity of the results to certain arbitrary changes in the trial function.

The effect of the variation of γ on the convergence of the phase shifts is illustrated in Table V. In the Case A singlet S -wave solution at $k=0.01$ the stationary point in γ occurs at $\gamma=0.71$. In Table V are given the c 's and resulting $\tan\eta$'s at $\gamma=0.71$ and 1.0 as the number of virtual states included is increased from 1s only to 1s, 2s, and 3s. For $\gamma=0.71$ the effect on c_1 of introducing the higher virtual states is small and $\tan\eta$ has effectively reached its final value.

For $\gamma=1.0$, the excited states come in strongly with a very large effect on c_1 , and there are relatively large changes in $\tan\eta$. It is probably reasonable to assume that for $\gamma=1.0$, the introduction of higher ns terms and possibly some angular terms (p, d, \dots virtual states) into the trial function would be needed to get convergence of $\tan\eta$ to its correct value, while these terms would have relatively little effect on $\tan\eta$ at the optimized value of γ .

Table VI contains $-a/k$ for singlet S scattering at $k=0.01$ and various values of γ while the number of c_n 's in the trial function is increased from one to three. These values are essentially the scattering lengths as there is very little change in going from $k=0.01$ to $k=0$. Since $-a/k$ does decrease uniformly as more parameters are added for any arbitrary fixed value of γ , it appears that the singlet scattering length as derived from our present trial function is an upper bound on the true value.

A criterion which has been used¹² for the correctness of the results of the Kohn method (our Case A) is the

TABLE VI. Values of $-a/k$ as a function of γ for singlet S wave at $k=0.01$ as the number of parameters in trial function is increased.

γ	With c_1	With c_1 and c_2	With c_1, c_2 , and c_3
0.2	9.940	9.936	9.929
0.4	9.791	9.764	9.736
0.6	8.371	8.362	8.357
0.8	8.331	8.287	8.286
1.0	8.680	8.596	8.445
1.2	9.124	8.641	8.634
1.4	9.554	8.974	8.955
1.6	9.923	9.333	9.284
1.8	10.22	9.660	9.594

closeness of the quantity a/a_i to unity. Our method of choosing the best stationary point at any given energy is equivalent to this, at least when applied to within Case A or Case B. It is probably not proper, however, to regard this test as a criterion in the absolute sense. At high energies, where the variational phase shifts are approaching the Born approximation values, the ratio a/a_i departs quite markedly from unity. For instance, at $k=6.0$, where both η_0^+ and η_0^- are well within 10% of the Born approximation, $(a/a_i)_+=0.313$ and $(a/a_i)_-=0.310$. In addition, this ratio will depart drastically from unity when η goes through zero, even though η is presumably correct (see results for η_1^+ and η_2^+ , $k=1.5$). This occurs because the correct a is identically equal to zero when $\eta=0$. A similar thing happens to b/b_i when η goes through $\pi/2$. This test is more likely a better indication of how well the trial function can be made to satisfy the Schrödinger equation over the space of the two electrons than of the accuracy of the resulting variational phase shift. Our trial function at these high

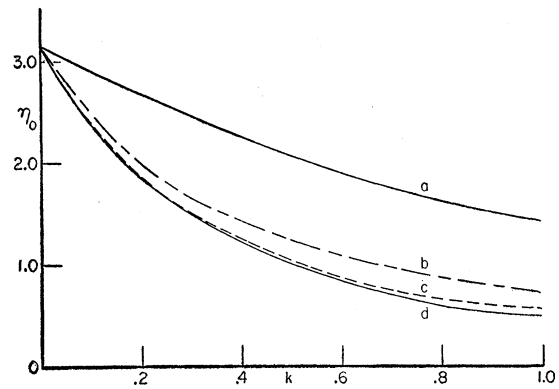


FIG. 2. S -wave phase shifts as a function of k . (a) Triplet phases; all calculations in good agreement. Singlet phases given by (b) BDJS, (c) Hartree-Fock method, and (d) this calculation.

energies is admittedly inadequate, but the presumably correct phase shifts are obtained, similar to what occurs in the variational energy calculations.

VII. DISCUSSION OF RESULTS

In Fig. 2 we compare our S phase shifts with the Hartree-Fock (or one-state exchange approximation) phases¹³ and with the variational phases of Bransden, Dalgarno, John, and Seaton.¹² We have plotted the adopted S -wave phases of BDJS, of which some were calculated by them and some by Massey and Moiseiwitsch.¹⁴ The triplet S phases all agree very well. In

¹³ The original calculation of the S -wave Hartree-Fock phases was made by P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933). Their paper contained an error and the corrected calculation for S and P waves has been done by K. Omidvar, New York University Institute of Mathematical Sciences Report No. CX-37 (unpublished), and T. L. John. I am grateful to Dr. John for sending me his results in advance of publication.

¹⁴ H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) A205, 483 (1951).

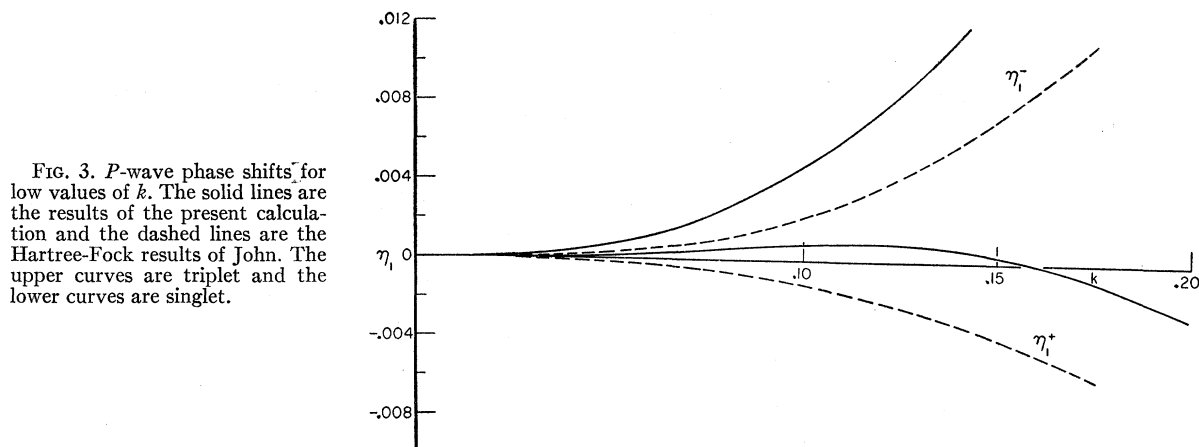


FIG. 3. P -wave phase shifts for low values of k . The solid lines are the results of the present calculation and the dashed lines are the Hartree-Fock results of John. The upper curves are triplet and the lower curves are singlet.

fact, our results agree with the Hartree-Fock triplet S phases to 4 significant figures at all energies up to $k=0.8$. While our singlet S phases are quite close to the Hartree-Fock values, they fall considerably below the adopted BDJS phases. Our value of 8.220 for A_0^+ compares with the Hartree-Fock value of 8.095 and the BDJS value of 7.02. Other calculated values^{1,15,16} for A_0^+ range between 6 and 10.

In the earlier variational calculations^{12,14} the introduction of an arbitrary function of r_{12} into the trial function is equivalent to the choice of a specific $\Phi_\lambda(r_1, r_2)$ in (14) for all λ , each of which is multiplied by the same variational parameter. This results in no flexibility to give more weight to some λ 's than to others, and may lead to an over estimate of the effect of the higher angular correlations.

Very recently there has been theoretical work on upper bounds for variationally determined scattering lengths by Ohmura and by Spruch and collaborators.¹⁷ Their conclusions depend very heavily upon the knowledge of the existence of *all* the bound states of the scattering system, i.e., in this case the singlet and triplet system of H^- . The only state of H^- whose existence is certain is the well-known singlet ground state bound by 0.75 ev. On the assumption of the existence of only the ground state of H^- , Rosenberg, Spruch, and O'Malley¹⁸ find the upper bounds $A_0^+ \leq 6.23$ and $A_0^- \leq 1.91$, which are in conflict with the present as well as many other theoretical results. As it is unlikely that other bound states exist¹⁹ this discrepancy in the scattering lengths remains unexplained.

¹⁵ T. Ohmura, Y. Hara, and T. Yamanouchi, *Progr. Theoret. Phys. (Kyoto)* **20**, 82 (1958).

¹⁶ S. Borowitz and H. Greenberg, *Phys. Rev.* **108**, 716 (1957).

¹⁷ T. Ohmura, *J. Math. Phys.* **1**, 27, 35 (1960); L. Spruch and L. Rosenberg, *Phys. Rev.* **117**, 1095 (1960); L. Rosenberg, L. Spruch, and T. F. O'Malley, *Phys. Rev.* **118**, 184 (1960).

¹⁸ L. Rosenberg, L. Spruch, and T. F. O'Malley, *Bull. Am. Phys. Soc.* **5**, 65 (1960), and *Phys. Rev.* **119**, 000 (1960).

¹⁹ I have been informed privately by Professor C. L. Pekeris that he has looked for a bound triplet state of H^- but did not find one [for method see C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958)]. If the order of the 2^1S levels in H^- are assumed to be the same

The P -wave results are particularly illuminating when compared with other calculations. For $k > 0.5$, our results for the singlet and triplet P phase shifts are in good agreement with the Hartree-Fock phases, the variational phases of BDJS (exchange approximation, no polarization), and those calculated by Malik. For $k < 0.5$, both our singlet and triplet phases become gradually shifted positively relative to the Hartree-Fock curves. This causes the singlet phase shifts to become positive again near zero energy (see Fig. 3). The absolute net change in η_1 is so small as to negligibly affect the scattering cross sections.

In their investigation of the effect of introducing a polarization term of arbitrary strength into the electron-hydrogen atom interaction, BDJS find that increasing the magnitude of the polarization term results in a positive shift of the entire P -wave phase-shift curve at all energies. Thus it becomes apparent that the trouble with the adiabatic approximation is that it introduces a constant polarization potential, whereas our results indicate it should be strongly energy dependent. Table VII illustrates the effect on η_1^+ of including more virtual excited states (the equivalent of more polarization) in the trial function. When the $2s$ and $3s$ states are excluded the resulting phase shift is identical to the Hartree-Fock value of -0.0012 at $k=0.1$. It appears that still further improvement could be expected with the inclusion of more terms in the trial function.

The only other published evaluation of the D -wave phase shifts is the Hartree-Fock calculation of

TABLE VII. Singlet P -wave results for $k=0.1$ and optimized γ in Case A as the number of virtual states is increased.

γ	c_1	c_2	c_3	η
1.01	-0.0001677	-0.001203
0.82	-0.01009	0.006314	...	-0.000343
0.80	-0.01120	0.006617	-0.003978	0.000817

as in He, the 2^1S state of H^- would also not be expected to be bound. However, this assumption may not be valid.

McEachran and Fraser.²⁰ The present values are of the same sign but larger in magnitude than theirs by the order of 30%.

Ohmura, Hara, and Yamanouchi¹⁵ have extended the effective range theory of neutron-proton scattering to the case of electron-hydrogen atom singlet scattering. Here $k \cot \eta_0^+$ is expanded in the form

$$k \cot \eta_0^+ = -\alpha + \frac{1}{2}\rho(\alpha^2 + k^2) + O[(\alpha^2 + k^2)^2], \quad (18)$$

where α^2 is the binding energy of the H^- ground state in rydbergs, 0.0555. The coefficient ρ is approximated from a knowledge of the bound-state wave function alone and is found to be 2.646 by Ohmura and Ohmura²¹ using the best available H^- wave function. When this value is inserted into (18) and the third term on the right neglected, $A_0^+ = 6.167$ is obtained. This is in significant disagreement with our value for A_0^+ , but consistent with the Rosenberg, Spruch, and O'Malley upper bound. Our variationally obtained values for $k \cot \eta_0^+$ cannot fit (18) unless the terms in $O[(\alpha^2 + k^2)^2]$ contribute appreciably. This is made apparent by noting in Fig. 1 that the extension of the limiting straight line for $k \cot \eta_0^+$ does not intersect the point corresponding to the bound state, $k \cot \eta_0^+ = -\alpha$ at $k^2 = -\alpha^2$. No estimate has been made of the magnitude of the higher terms, and

they may be large due to the presence of exchange, which does not enter the neutron-proton scattering problem. Also the validity of the approximation used to obtain ρ is somewhat uncertain and would surely break down if an excited bound singlet state existed.

The total elastic cross section resulting from our phases is consistent with the experimental result of Brackmann, Fite, and Neynaber²² below 10 eV, but much more precise experimental data, in particular for the angular distribution of elastic scattering, are needed in order to choose between the various calculations of phase shifts.

In conclusion, we cannot quantitatively estimate the error in our phase shifts arising from inadequacies in the trial function. However, for reasons discussed in Secs. III and V it is our feeling that this error is small. It is apparent that further theoretical study of the possible existence of excited states of H^- would be very important in clarifying the low-energy scattering situation.

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²⁰ R. P. McEachran and P. A. Fraser, Can. J. Phys. **38**, 317 (1960). *Note added in proof.*—The as yet unpublished Hartree-Fock D -wave results of T. L. John and A. Temkin and J. C. Lamkin have recently come to our attention. They agree with each other and are also very close to the present results. Thus the McEachran and Fraser D -wave phase shifts are probably in error by about 30%.

²¹ T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960). My thanks are due to Dr. Ta-You Wu for giving me preprint copies of this paper and the ones by T. Ohmura cited in reference 17.

²² R. T. Brackmann, W. L. Fite, and R. H. Neynaber, Phys. Rev. **112**, 1157 (1958).