

## Electron-Hydrogen Scattering Calculation

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Elastic electron-hydrogen scattering phase shifts for  $L=1$  are calculated from the Kohn variational principle, using up to 84 "Hylleraas-type" trial functions. Accuracy of the resulting phases varies from one to four significant figures, depending on the energy. A resonance appears in the  $^3P$  wave at 9.727 eV. Elastic  $P$ -wave positron-hydrogen phase shifts are also calculated.

### INTRODUCTION

THE purpose of this paper is to report some accurate numerical calculations of elastic  $P$ -wave phase shifts for electrons scattered from hydrogen atoms. We have applied the Kohn variational principle in the same systematic fashion that Schwartz<sup>1,2</sup> applied it to  $S$ -wave scattering, taking the physical model to be an electron incident on a ground-state hydrogen atom having an infinitely massive nucleus. Only Coulomb forces are included in the Hamiltonian, but the two-electron wave function is explicitly symmetric (singlet) or antisymmetric (triplet) to account completely for exchange. Within this framework no approximations have been made.

### VARIATIONAL PROCEDURES

Our starting point is the Kohn variational principle,<sup>3</sup>

$$[\lambda] = \lambda - 2 \int \Psi (H - E) \Psi d\tau_1 d\tau_2, \quad (1)$$

where

$$2(H - E) = -\nabla_1^2 - \nabla_2^2 + 2/r_{12} - 2/r_1 - 2/r_2 + 1 - k^2,$$

and  $\lambda = (\tan\eta)/k^2$ . The trial wave function is  $\Psi = \phi + \chi$  for the  $P$  wave, where

$$\phi = (1 \pm P_{12}) e^{-r_2} \{ j_1(kr_1) - \tan\eta [j_2(kr_1) + (2/kr_1) j_3(kr_1)] \} \hat{r}_1 (2/k)^{1/2} / 4\pi, \quad (2)$$

and

$$\chi = \sum_{l+m+n \leq N} C_{lmn} e^{-(\kappa/2)(r_1+r_2)} r_{12}^l \times (r_1^m r_2^n \mathbf{r}_1 \pm r_1^n r_2^m \mathbf{r}_2) / \sqrt{2}. \quad (3)$$

In these formulas,  $k^2$  is the kinetic energy of the incident electron in rydbergs,  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ,  $P_{12}$  interchanges  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ,  $\hat{r}_1$  is a unit vector, and  $j_l$  is the spherical Bessel function of order  $l$ . The expression in the square brackets multiplying  $\tan\eta$  in (2) has the same asymptotic behavior as the spherical Neumann function<sup>4</sup>  $n_1(kr)$

through order  $1/r^2$  but, unlike  $n_1$ , is regular at the origin. Powers of  $k$  are distributed in such a way that the stationary quantity  $[\lambda]$  approaches a nonzero constant as  $k \rightarrow 0$ .<sup>5</sup>

To find a phase shift at one energy, the quantity  $[\lambda]$  in Eq. (1) is made stationary by variations of the parameters  $\lambda$  and  $C_{lmn}$  for a given  $N$  and  $\kappa$ , a simple linear problem. Then  $N$  is increased by 1 and the process repeated. Usually these successive  $[\lambda]$  form an obviously convergent sequence, and we may extrapolate by inspection to  $N = \infty$ . However, it is possible for the sequence to diverge or to converge speciously at any one  $\kappa$ . (Bound-state variational problems carry a guarantee that an increase in flexibility of the trial function will improve the results,<sup>6</sup> but scattering problems in general do not.<sup>1</sup>) Following Schwartz, the calculation is repeated for several values of  $\kappa$  and the convergent behavior of the sequence mapped out.

Most of the calculations were done for  $N=1, 2, 3, 4$ , and 5, yielding 4, 10, 20, 35, and 56 terms, respectively, in  $\chi$ ; however, in the region  $k^2=0.696$  to 0.720 we have gone up to  $N=6$  (84 terms) for improved accuracy.

### RESULTS

Figures 1 and 2 represent  $P$ -wave triplet and singlet "maps" for the lowest  $e$ -H energy studied,  $k^2=0.01$  (0.136 eV). The scale parameter  $\kappa$  is measured along the horizontal axis. These curves have a smooth parabolic behavior, with no apparent singularities; there may well be singularities that a finer partition of  $\kappa$  would uncover, but the structure is clear enough for our purpose. (Each of the arrows in the figures points to the best value of  $[\lambda]$  for corresponding  $N$ .) At this low energy the interaction is mainly due to polarization

As  $k$  is increased, the character of the curves changes, as seen in Figs. 3 and 4 for  $k=0.5$ . There is a marked flattening as  $N$  is increased, singularities appear (the dashed portions), and convergence (ignoring the singularities) is better. This improved convergence with increasing  $k$  may be understood by looking at the form of a

fore correct only through  $0(1/r^2)$ . We leave it to the flexible function  $\chi$  to handle the polarization effects.

<sup>5</sup> T. F. O'Malley, L. Spruch, and L. Rosenberg [J. Math. Phys. 2, 491 (1961)] have shown that  $\tan \eta_L \rightarrow \alpha \pi k^2 [(2L+3)(2L+1) - (2L-1)]^{-1}$  as  $k \rightarrow 0$  for the  $L$ th partial wave, where  $\alpha$  is the polarizability. For hydrogen  $\alpha = \frac{9}{2}$ .

<sup>6</sup> J. K. L. MacDonald, Phys. Rev. 43, 830 (1933); E. A. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930).

<sup>1</sup> Charles Schwartz, Phys. Rev. 124, 1468 (1961).

<sup>2</sup> C. Schwartz, Ann. Phys. (N. Y.) 16, 36 (1961).

<sup>3</sup> W. Kohn, Phys. Rev. 74, 1763 (1948).

<sup>4</sup> If the electron-atom force were short range, then  $n_1$  would have exactly the correct asymptotic behavior. However, the polarization potential goes like  $-\alpha/r^4$  far away [see, for example, L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc. (London) A254, 259 (1960)], and it is easy to see that  $n_1$  is there-

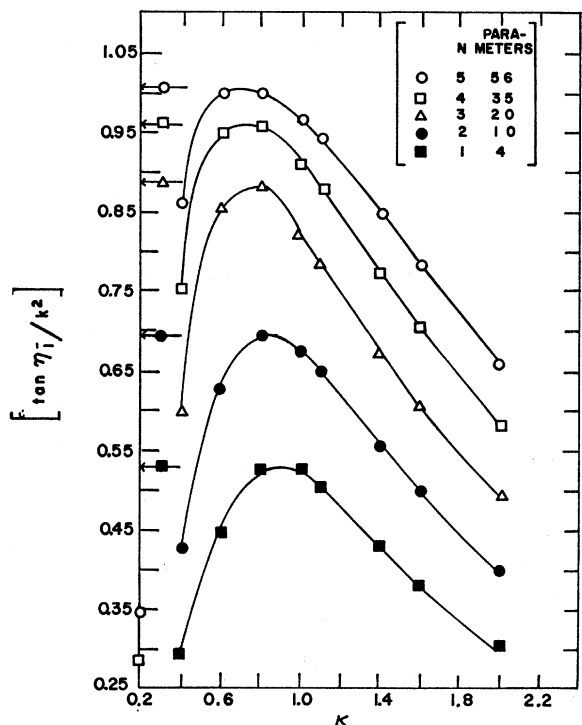


FIG. 1. Triplet  $P$  at  $k=0.1$ . Arrows indicate the best  $[\lambda]$  for each  $N$ .

typical basis function  $u_n = e^{-kr}r^n$ . It has a maximum at  $r_0 = n/\kappa$  and then rapidly tails off to zero as  $r$  increases. The dominant error term in the wave function is something like  $\sin(kr)/r^3$ ; for small  $k$  this error term is a slowly oscillating function with decreasing amplitude as  $r$  increases, which the  $u_n$  cannot easily duplicate. At

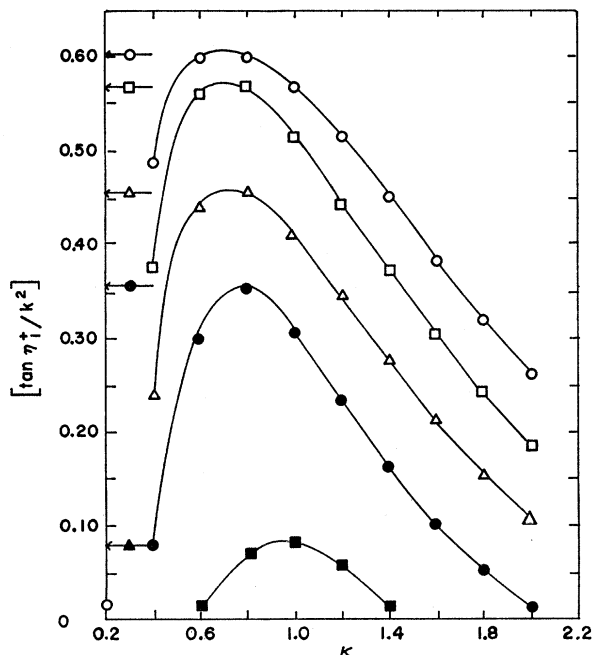


FIG. 2. Singlet  $P$  at  $k=0.1$ .

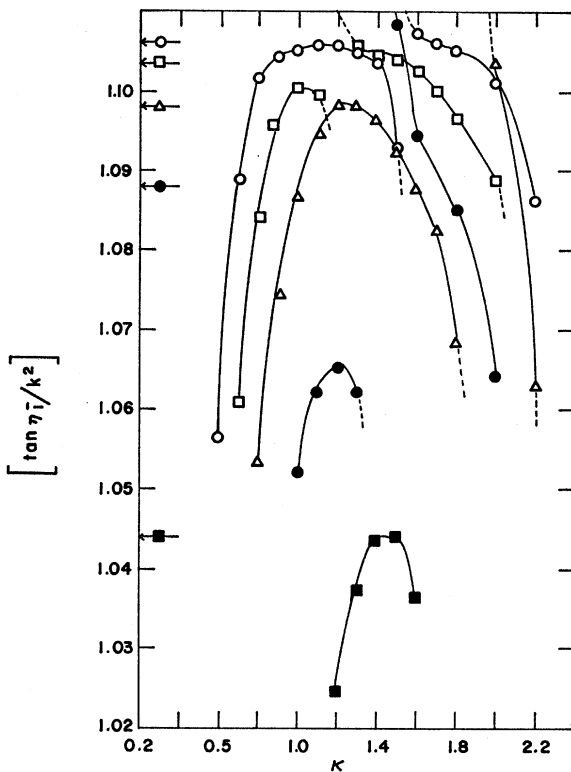


FIG. 3. Triplet  $P$ ,  $k=0.5$ .

larger  $k$  the oscillations are faster, and successive oscillations more nearly cancel to give an "average" function

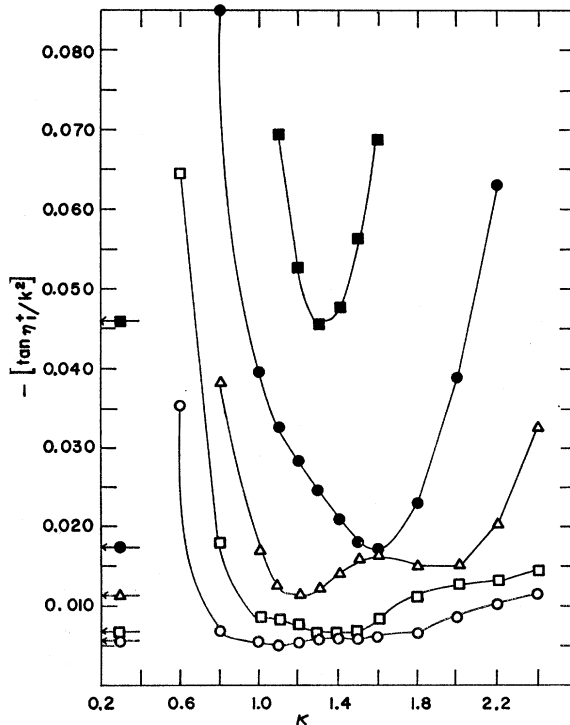


FIG. 4. Singlet  $P$  at  $k=0.5$ .

that vanishes rapidly as  $r \rightarrow \infty$ . The  $u_n$ , whose purpose is to remove the error, therefore have an easier task.<sup>7</sup>

As the energy approaches the excitation threshold ( $k^2 = \frac{3}{4}$ ) convergence deteriorates for another reason.<sup>1</sup> For  $k^2 > \frac{3}{4}$ , the asymptotic part of the wave function has a term  $e^{ik'r}$ , where  $k' = (k^2 - \frac{3}{4})^{1/2}$ . For  $k^2$  slightly less than  $\frac{3}{4}$ ,  $k'$  is a small imaginary number  $i\epsilon$ , and the wave function should have a term which behaves as  $e^{-\epsilon r}$ . For small positive  $\epsilon$  this is a long tail and not easily duplicated by the short-range functions.

Between  $k^2 = 0.714$  and  $0.716$  (9.71 and 9.74 eV), our calculations show a sudden rise in the triplet  $P$ -phase shift, corresponding closely to a  $^3P$  compound-atom level calculated by O'Malley and Geltman<sup>8</sup> at 9.727 eV above the ground state of H, and to a resonant structure at  $9.71 \pm 0.03$  eV found experimentally by McGowan *et al.*<sup>9-11</sup> Unfortunately, our calculations do not converge in the vicinity of the O'Malley-Geltman  $^1P$  resonance at  $k^2 = 0.7481$ .

In all cases  $[\lambda]$  increases monotonically with  $N$ . (See Figs. 1 through 4.) Therefore, while we cannot prove it, we believe that  $\eta$  calculated for the largest  $N$  (5 or 6 in the  $e^-H$  case) is a lower bound on the correct  $\eta$ , and it is so tabulated in Table I in row (a). Row (b) is the most probable value for the phase, obtained by extrapolating to  $N = \infty$ . Gailitis<sup>12</sup> has used a variational method (equivalent to one devised by Hahn *et al.*<sup>13</sup>) to calculate the  $L=1$  phase shift, and we have tabulated his results alongside our own for comparison.<sup>14</sup> His  $^3P$  phases appear to be quite accurate and in addition provide the security of a lower bound. However, there is a significant disagreement in the singlet case.

It would be convenient to take the difference between  $[\lambda]$  and  $\lambda$  as a measure of the accuracy of such a variational calculation; however, while it is usually true that  $|[\lambda] - \lambda|$  is smallest in the region of  $\kappa$  where the curves are stationary, this quantity passes through zero and could easily lead to an overestimate of the accuracy.

<sup>7</sup> Schwartz shows that a variational scheme employing Laguerre polynomials to represent a function with asymptotic form  $1/r^d$  may be expected to converge as  $\sum 1/N^{2d-d}$ , where the volume element is  $r^d dr$ . This gives a convergence of  $\sum 1/N^4$  for our problem. Although Schwartz's model is only approximately related to our calculation, this agrees reasonably well with a crude numerical analysis of our convergence at low energy. See C. Schwartz, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 241.

<sup>8</sup> T. F. O'Malley and S. Geltman, *Phys. Rev.* **137**, 1344 (1965).

<sup>9</sup> J. William McGowan, E. M. Clarke, and E. K. Curley, *Phys. Rev. Letters* **15**, 917 (1965); **17**, 66 (1966).

<sup>10</sup> J. William McGowan, *Phys. Rev. Letters* **17**, 1207 (1966).

<sup>11</sup> J. William McGowan, *Phys. Rev.* **156**, 165 (1967).

<sup>12</sup> M. Gailitis, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Inc., Hastings-on-Hudson, N. Y., 1965).

<sup>13</sup> Y. Hahn, T. F. O'Malley, and L. Spruch, *Phys. Rev.* **130**, 381 (1963).

<sup>14</sup> For another good calculation of  $e^-H$   $P$ -wave phases, see I. H. Sloan, *Proc. Roy. Soc. (London)* **A281**, 151 (1964). Sloan bases his calculation on the method of polarized orbitals, for which see A. Temkin and J. C. Lamkin, *Phys. Rev.* **121**, 788 (1961).

TABLE I. Elastic phase shifts for  $L=1$ , electron-hydrogen triplet ( $\eta_1^-$ ) and singlet ( $\eta_1^+$ ), and positron-hydrogen ( $\eta_1$ ). Entries are in radians, modulo  $\pi$ . Row (a) is the probable lower bound and (b) the most probable value, where the number in parentheses refers to the likely error in the preceding digit. The lower bounds calculated by Gailitis for  $\eta_1^-$  and  $\eta_1^+$  are taken from Ref. 12.

$k^2$ (rydbergs)	$\eta_1^-$		$\eta_1^+$		$\eta_1$
	Present work	Gailitis	Present work	Gailitis	Present Work
0.01	(a) 0.0101		0.006	0.0046	0.008
	(b) 0.0114(6)		0.007(1)		0.009(1)
0.04	(a) 0.0448	0.045	0.0146	0.0142	0.032
	(b) 0.0450(1)		0.0147(2)		0.033(1)
0.09	(a) 0.1059		0.0163		0.064
	(b) 0.1063(2)		0.0170(2)		0.065(1)
0.16	(a) 0.1866	0.186	0.0096	0.0079	0.099
	(b) 0.1872(3)		0.0100(2)		0.102(1)
0.25	(a) 0.2700	0.271	-0.0014	-0.0037	0.130
	(b) 0.2705(3)		-0.0007(5)		0.132(1)
0.36	(a) 0.3405		-0.010		0.153
	(b) 0.3412(3)		-0.009(1)		0.156(2)
0.49	(a) 0.3918	0.390	-0.014	-0.0178	0.175
	(b) 0.3927(5)		-0.013(2)		0.178(3)
0.64	(a) 0.425	0.424	-0.005	-0.0104	
	(b) 0.427(5)		-0.004(1)		
0.696	(a) 0.442		0.003		
	(b) 0.447(5)		0.005(2)		
0.712	(a) 0.486		0.006		
	(b) 0.49(1)		0.008(2)		
0.713	(a) 0.508				
	(b)				
0.714	(a) 0.553				
	(b)				
0.715	(a) 0.713		0.0073		
	(b) 0.72(1)		0.008(1)		
0.716	(a) 2.89				
	(b)				
0.720	(a) 0.44	3.34	0.009	0.0017	
	(b) 0.45(1)		0.010(3)		
0.7396	(a)		0.019		
	(b)		0.03(1)		
0.75	(a) 0.44		0.054		
	(b) 0.44(2)				

## POSITRON-HYDROGEN SCATTERING

A few changes in the computer program enabled us to calculate elastic  $P$ -wave phase shifts for  $e^+H$  scattering. The first inelastic channel appears at  $k^2 = 0.5$ , corresponding to positronium formation, so calculations extend only up to  $k = 0.7$ . The positron results are not as accurate as the electron results, because removing the wave-function (anti)symmetry doubles the number of short-range functions for a given  $N$  and forces us to stop at  $N = 4$ . The close-in function becomes

$$\chi = \sum_{l+m+n \leq N} e^{-(\kappa/2)(r_1+r_2)} r_{12}^l \times [C_{lmn} r_1^m r_2^n \mathbf{r}_1 + D_{lmn} r_1^n r_2^m \mathbf{r}_2].$$

The results appear in Table I.<sup>15</sup>

## ACKNOWLEDGMENT

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<sup>15</sup> Compare, for example, C. J. Kleinman, Y. Hahn, and L. Spruch, *Phys. Rev.* **140**, A413 (1965); also R. J. Drachman, *ibid.* **138**, A1582 (1965).