Nonadiabatic Theory of Electron-Hydrogen Scattering. II

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The triplet S-wave electron-atomic hydrogen elastic scattering phase shifts are recalculated by a previously introduced nonadiabatic theory. The previous calculation has been improved in a number of respects the most important of which is the utilization of noniterative technique for numerically solving the partial differential equations. (This technique is expected to be useful for a large class of linear second-order elliptic partial differential equations.) Phase shifts are computed to better than four significant figures. The results are quite close to the variational results of Schwartz but on the whole somewhat larger. The deviations are considered significant, and the various approaches are discussed. Specifically our triplet scattering length (in Bohr radii) is $a_t=1.7683$, with an extrapolated value $a_t=1.767$.

I. INTRODUCTION

THE extension of the relative partial wave treatment to the (electron-hydrogen) scattering problem was introduced[1] to allow for the calculation of phase shifts of sufficient accuracy for experimental purposes and to allow for meaningful comparison by approximate theories. The completion of the original program[2] has apparently met the purposes for which it was intended.[3]

With regard to the original calculation it was clear from the first[4] that the devices that were introduced to elicit information about the higher order corrections, which, exactly, involved the solutions of two-dimensional partial differential equations, limited the accuracy to significantly less than that to which the method was intrinsically capable. In addition a variational calculation[5] has appeared in which the estimated accuracy was much higher than in reference 2.

The variational calculation utilized (in Kohn's variational principle) a Hylleraas-type wave function with an increasingly large number (N) of parameters. The estimate of the error was based on the device, first exploited by Pekeris,[6] of observing the results as a function of N. However the variational calculations pertaining to scattering are not compelling to the accuracy claimed for at least two reasons. First the variational results at nonzero energies show a kind of wild behaviour as a function of the nonlinear parameter which has required a very intuitive method of interpretation.[7] (For $k>0$ one does not have the cushion of a guaranteed lower bound on the phase shifts.) More important, however, is the fact that a Hylleraas wave function does not naturally describe the complete wave function corresponding to a scattering problem. At zero energy, in fact, it has conclusively been demonstrated[8] that the long-range adiabatic tail is essential for highly quantitative purposes. Although the variational calculation in its final stages did include such a term at zero energy, it did not include it for nonzero energies; it is still very much in question to what extent this term enters at small but finite energies.

For these reasons it has seemed necessary to carry out our intention of numerical integration for the higher order correction. The calculation has been restricted to the triplet case as discussed in the next section. In Sec. III we discuss the method of numerically integrating the partial differential equations. Finally in Sec. IV we present results and discussion.

II. REVIEW OF THE NONADIABATIC THEORY

It will be recalled that the nonadiabatic theory starts with a decomposition of the S-wave function

$$\Psi(r_1r_2\theta_{12})=\frac{1}{r_1r_2}\sum_{l=0}^{\infty}(2l+1)^{1/2}\Phi_l(r_1r_2)P_l(\cos\theta_{12}), \quad \text{(I2.3)}$$

from which by substitution into the Schrödinger equation an infinite set of coupled two-dimensional partial differential equations (I2.4) results. One defines a zeroth order problem by neglecting the coupling terms of the $l=0$ equation:

$$\left(\Delta_{12}+E+\frac{2}{r_2}\right)\Phi_0^{(0)}(r_1r_2)=0, \quad \text{(I3.3)}$$

where

$$\Delta_{12}\equiv\partial^2/\partial r_1^2+\partial^2/\partial r_2^2.$$

The zeroth-order wave function; $\Phi_0^{(0)}$, is required to have the asymptotic boundary condition corresponding to a scattered wave:

$$\lim_{r_1\to\infty}\Phi_0^{(0)}(r_1r_2)=\sin(kr_1+\delta_0)R_{1s}(r_2). \quad \text{(I3.4)}$$

δ_0 is the zeroth-order phase shift, and it can be interpreted as the phase shift of a rudimentary type of three-body problem, to which it turns out, many previous approximations were unknowingly addressed.

[1] A. Temkin, Phys. Rev. Letters **4**, 566 (1960). This method is called the "nonadiabatic theory."
[2] A. Temkin, Phys. Rev. **126**, 130 (1962). This paper will be referred to as I. Equations referring to it will be prefixed by a I.
[3] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).
[4] Cf. reference 2, footnote 17.
[5] C. Schwartz, Phys. Rev. **124**, 1468 (1961).
[6] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958), and subsequent papers.
[7] C. Schwartz, Ann. Phys. (N. Y.) **15**, 36 (1961).
[8] A. Temkin, Phys. Rev. Letters **6**, 354 (1961).

The basic relation of the nonadiabatic-theory is given by

$$\sin(\delta-\delta_0)=-\frac{1}{k}\sum_{l=1}^{\infty}\frac{2}{(2l+1)^{1/2}}\times\int_0^{\infty}dr_1\int_0^{r_1}dr_2\,\Phi_0^{(0)}\frac{r_2{}^l}{r_1{}^{l+1}}\Phi_l, \quad \text{(I3.5)}$$

where δ is the exact s-wave phase shift. The integration domain is confined to the region $r_1\geq r_2$. The convergence of the terms on the right-hand side was established by noting that the significant contribution to each integral comes from two regions. One is the adiabatic region, $r_1\gg r_2$ and r_2 small. We shall have much to say about this contribution in connection with the shortcomings of the Hylleraas wave function variational approach, however for the purposes of the present nonadiabatic theory these contributions can readily be accounted for, and can be shown to go down rapidly as a function of l. The other region which must be considered is for intermediate values of r_1 and r_2. This gives the essential contribution to the deviation of δ from δ_0. The convergence of this contribution can be made plausible by noting that each Φ_l equation has a centrifugal barrier term $-l(l+1)(r_1^{-2}+r_2^{-2})$ which successively diminishes the amplitude of Φ_l in that region. This argument is analogous to the argument that the contributions of successive partial waves go down for low impacting energies in the complete description of the scattering process. It should be emphasized, however, that there is not a one-to-one correspondence in this analogy, for the equations of partial waves are uncoupled, whereas the relative partial wave equations are coupled. Thus, whereas one can assert rigorously that only partial S waves contribute to the zero-energy cross section, it is not true that only the S relative angular momentum state contributes to the S-wave phase shift at zero energy. What is here being asserted is that the contributions from higher relative angular momentum states diminish in a usefully convergent manner.

There is an additional circumstance, which was not really emphasized in I, which renders the argument of convergence particularly cogent in the triplet case. In that case we have the boundary conditions

$$\Phi_l(r_1=r_2)=0, \quad l=0, 1, \cdots \quad \text{(I2.6)}$$

$$\Phi_0^{(0)}(r_1=r_2)=0. \quad \text{(I4.3)}$$

From inspection of (I3.5) one can see, by virtue of the $r_2{}^l/r_1{}^{l+1}$ factor, that the region $r_2\gtrsim r_1$ would tend to become increasingly important for the higher relative partial waves. However because of the boundary condition, the contribution from this region must in fact be small; therefore the main contribution to each integral must come from r_2 significantly less than r_1. But in that region $r_2{}^l/r_1{}^{l+1}$ certainly diminishes rapidly as a function of l. Thus one has every reason for believing the convergence will be exceedingly rapid in the triplet case. The same arguments should also render our perturbation theory

$$\Phi_l=\sum_{i=0}^{\infty}\lambda^{i+l/2}\Phi_l{}^{(i)}$$

particularly effective.

TABLE I. Zeroth order double precision results for $k=0.2$ atomic unit (a.u.).

Expansion	Determinant	Diagonal sum	δ_0
2	0.154×10^{-1}	0.358×10^{-2}	2.71098
2, 3	0.315×10^{-6}	0.141×10^{-4}	2.679565
2, 3, 4	0.541×10^{-14}	0.231×10^{-6}	2.6794215
2, 3, 4, 5	0.418×10^{-25}	0.137×10^{-8}	2.6794197
2, 3, 4, 5, I_0	0.246×10^{-36}	0.553×10^{-7}	2.67962
2, 3, I_0	0.621×10^{-12}	0.823×10^{-7}	2.6794200
2, 3, I_0, I_1	0.329×10^{-16}	0.142×10^{-7}	2.6794192
2, 4, I_0	0.123×10^{-12}	0.773×10^{-8}	2.6794191
2, 4, I_0, I_5, I_{10}, I_{20}	0.638×10^{-26}	0.742×10^{-8}	2.6794191

These reasons plus the calculated values which are presented below give a strong expectation that including through quadratic terms, will yield more than four place accuracy in the phase shifts. This accuracy is required in order meaningfully to be compared with Schwartz's results.

The original calculation has been improved in two main respects. Firstly we have generalized the zeroth order technique of solution to double precision arithmetic on the IBM 7090 computer of the Theoretical Division of the Goddard Space Flight Center. In the single precision program we were plagued with vanishing determinants which used up very rapidly all the 8 significant figures that the machine could store. In the double precision program the 16 significant figures were sufficient to yield zeroth-order phase shifts from better than 4 to almost 8 significant figures.

To illustrate the gain in accuracy of our zeroth-order results by making the program double precision, we present in Table I a typical set of results for $k=0.2$. The middle two columns refer to quantities labeled "det" and I_T in I. The first of these gives an indication of the number of significant figures lost in the evaluation of the determinant det. For example in the row corresponding to the expansion 2, 3, 4, 5, the main diagonal of det, $\prod_{i=1}^{4}(\mathrm{ME})_{ii}$, is approximately equal to 0.6×10^{-9}, figuring an average of 0.5×10^{-2} as the average value of a diagonal matrix element. Comparing this with 0.42×10^{-25}, the actual value of the determinant, we see that approximately 16 significant figures have been lost. This is the maximum that the double precision arithmetic affords, and the conclusion is reinforced by referring to the next row, 2, 3, 4, 5, I_0. Here almost 25 significant figures have been lost, and the corresponding diagonal sum increases. If the elements of the calculation have sufficient (infinite) accuracy, it is clear that the addition of a term to an expansion can only decrease

the diagonal sum. Thus the δ_0 for that expansion is very unreliable. In each of the groups of rows separated by blank rows each subsequent row augments the previous one by an additional term, and except for the above-noted case the diminishing of diagonal sums occurs. This should be compared with Table III of Temkin and Hoover[9] in which a similar set of results based on a single precision program was presented. There an increase in the diagonal sum occurred in third row. In the present case, we could with some legitimacy claim $\delta_0=2.6794194(3)$; however the value $\delta_0=2.67942$ is quite adequate for our purposes.

The main advancement we have achieved in the way of computing the complete S-wave phase shifts is the numerical integration of the higher order equations. These are elliptic equations, and it is well known that the usual way of numerically solving an elliptic equation is by some sort of relaxation or iteration technique. The novel feature of the technique we have used is that it is not iterative. Because it has worked where a relaxation technique has utterly failed to converge, and because it is applicable to a whole class of linear second-order equations, we have given some detail in the next section to the numerical solution.

III. SOLUTION OF THE PARTIAL DIFFERENTIAL EQUATIONS

The higher order effects in our expansion are given by the formula

$$\sin(\delta-\delta_0)=-\frac{1}{k}\sum_{\nu=1}^{\infty}\lambda^{\nu}\sum_{\substack{m+\mu=\nu\\ m\geq 1,\ \mu\geq 0}}2(2m+1)^{-1/2}\times\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^{m}}{r_1^{m+1}}\Phi_m^{(\mu)}dr_1dr_2. \quad \text{(I5.6)}$$

(For the purposes of the discussion in Sec. IV we emphasize that this λ expansion is a modification of the ordinary l expansion in relative partial waves, which is expected to hasten the convergence in the triplet case. It also has additional advantages discussed in I.)

The partial differential equation for $\Phi_0^{(0)}$ has been repeated in Sec. II. We repeat here the remaining equations:

$$[\Delta_{12}-2(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_1^{(0)}=2(3)^{-1/2}r_2r_1^{-2}\Phi_0^{(0)}, \quad \text{(I5.2)}$$

$$[\Delta_{12}+2r_2^{-1}+E]\Phi_0^{(1)}=2(3)^{-1/2}r_2r_1^{-2}\Phi_1^{(0)}, \quad \text{(I5.3)}$$

$$[\Delta_{12}-6(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_2^{(0)}=2(5)^{-1/2}r_2^{2}r_1^{-3}\Phi_0^{(0)}, \quad \text{(I5.4)}$$

$$[\Delta_{12}-2(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_1^{(1)}-\tfrac{4}{5}r_2^{2}r_1^{-3}\Phi_1^{(0)}=2(3)^{-1/2}r_2r_1^{-2}\Phi_0^{(1)}+4(15)^{-1/2}r_2r_1^{-2}\Phi_2^{(0)}. \quad \text{(I5.5)}$$

[9] A. Temkin and D. E. Hoover, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg [Academic Press Inc., New York (to be published)], Vol. I.

In principle these equations are to be integrated over the infinite region $0\leq r_2\leq r_1<\infty$. In practice, of course, one can only integrate up to a finite point $r_1=R$. If R is suitably large, one can perform the integrals in (I5.6) from R to ∞ by replacing the functions by their adiabatic forms:

$$\Phi_0^{(0)}\cong\sin(kr_1+\delta_0)R_{12}(r_2), \quad \text{(I4.2)}$$

$$\Phi_l^{(0)}=-\frac{2\sin(kr_1+\delta_0)}{(2l+1)^{1/2}r_1^{l+1}}e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right), \quad l=1,2 \quad \text{(I5.10)}$$

$$\Phi_1^{(1)}=-\frac{2}{\sqrt{3}}(\Delta\delta_0)\frac{\cos(kr_1+\delta_0)}{r_1^{2}}e^{-r_2}\left(\frac{r_2^{3}}{2}+r_2^{2}\right). \quad \text{(I5.11)}$$

The δ_0 being known, these equations with $r_1=R$ then define the boundary conditions on the numerical solution in the region $0\leq r_2\leq r_1\leq R$. It must be emphasized that as long as R is finite there is an approximation involved in these equations as boundary conditions. For these forms require not only $R\rightarrow\infty$, but also that $r_2\ll R$. However for numerical purposes one must know the boundary conditions for all values of $r_2\leq R$; the most natural thing to do is simply to use the above equations for all values of r_2. If R is large enough, one can be sure that the error thus incurred is very small, because in the region $r_2\lesssim R$ both the above functions and the true functions will be negligibly small.

The important question concerning R is how large is large enough? The time required for numerical integration effectively limited us to an $R=10$. It was our original intention to use the numerically integrated $\Phi_0^{(0)}$ in the quadratures (I5.6) together with the remaining numerically integrated functions. Our suspicion in this regard was aroused when at $k=0.4$ we found that

$$\int_0^{R}\int_0^{r_1}\frac{r_2}{r_1^{2}}(\Phi_0^{(0)})^{2}dr_1dr_2$$

was half the value that we got using the analytic expansion of $\Phi_0^{(0)}$ that we had as a by-product of the calculation of δ_0. We were therefore led to examine the deviation of our original $\Phi_0^{(0)}$,

$$\Phi_0^{(0)}=\sin(kr_1+\delta_0)R_{1s}(r_2)+\left(\sum_n+\int dp\right)C_ne^{-\kappa_nr_1}R_{ns}(r_2), \quad \text{(I4.4)}$$

from the boundary values imposed on the numerical solution via (I4.2). The results are given in Table II.

The important thing to notice is that the values along the line $r_1=10$ coming from the analytic $\Phi_0^{(0)}$ change sign at $r_2\cong 5$ whereas those defined by (I4.2), being proportional to $R_{1s}=2r_2e^{-r_2}$, do not. We concluded that this change of sign which was not taken care of in the

TABLE II. Comparison of boundary values at $r_1=10\ a_0$ ($k=0.4$ a.u.).

r_2 (a_0)	1	2	3	4	5	6	7	8	9	10
$\Phi_0^{(0)}(10,r_2)$	−0.01913	−0.01363	−0.00685	−0.00259	−0.00042	0.000486	0.000722	0.000612	0.000334	−0.000003
$\sin(10k+\delta_0)R_{1s}(r_2)$	−0.01853	−0.01363	−0.00752	−0.00369	−0.00170	−0.000749	−0.000321	−0.000135	−0.0000056	0[a]

[a] The expression on the left is not 0 at this point; however, for the purposes of numerical integration this point, being at $r_2=r_1$, was automatically taken as zero by our program.

boundary condition (I4.2) was responsible for the inaccuracy of the numerically integrated $\Phi_0^{(0)}$.

The double integral in which we observed the discrepancy is, of course, part of the dipole "sum rule"

$$\int_0^\infty\int_0^{r_1}\Phi_0^{(0)}\left[-2\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\right]\Phi_1^{(0)}dr_1dr_2 = \frac{2}{\sqrt{3}}\int_0^\infty\int_0^{r_1}(\Phi_0^{(0)})^2\frac{r_2}{r_1^2}dr_1dr_2. \quad \text{(I5.14)}$$

In the original calculation we used this relation to find the nonadiabatic effects of $\Phi_1^{(0)}$. In the present case, (I5.14) together with its counterpart for $\Phi_2^{(0)}$, plus additional sum rules that one can derive, serve as a check of the numerical integration. Now in the above noted case it was observed that the $\Phi_1^{(0)}$ found from (I5.2) using the incorrect $\Phi_0^{(0)}$ gave approximate equality in the sum rule. At work here was undoubtedly the phenomenon that the (incorrect) $\Phi_0^{(0)}$ is an important enough inhomogeneous term in the differential equation to influence $\Phi_1^{(0)}$ to be incorrect in just such a way as to give equality in (I5.14). This experience prevented any complacency on our part that the satisfaction of sum rules of the numerical function was a foolproof guarantee that the functions were correct.

The $k=0.4$ case is extreme in the sense that at no other energy have we observed the analytic $\Phi_0^{(0)}$ to change sign in such a prominent place along the boundary. (The change apparently stems from the fact that $\Phi_0^{(0)}$ has a node very close to $r_1=10$ at this energy.) Accordingly the differences between the integrals on the right-hand side of (I5.14) using the numerical versus the analytic $\Phi_0^{(0)}$ at other energies differed only in the second significant figure. However since we require practically three significant figures in the integral

$$\Delta\delta_0=-\frac{1}{k}\left[\int_0^{10}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2}{r_1^2}\Phi_1^{(0)}dr_1dr_2 + \int_{10}^\infty\int_0^{r_1}\Phi_0^{(0)}\frac{r_2}{r_1^2}\Phi_1^{(0)}dr_1dr_2\right], \quad \text{(I5.7)}$$

we could not use the numerically integrated $\Phi_0^{(0)}$.

We therefore decided to use the $\Phi_0^{(0)}$ gotten from the best expansion (I4.4) we had, and numerically integrate for the remaining functions. Our unfortunate experience with the dipole sum rule gave us some confidence that having a reliable $\Phi_0^{(0)}$ would make up for any deficiencies in the boundary conditions for the other functions. The sum rules, of course, still are a necessary condition to be satisfied; however, in view of the numerical integrals having to be cut off at R, they did not afford a critical test of the accuracy. We found that we did have to go a mesh size $h=0.1$ to get reasonable results. The most natural tests of accuracy, further halving the mesh size, integrating out to double the value of R, etc., were precluded by machine storage and particularly time considerations. As it was, it took ninety minutes to integrate a differential equation on the IBM 7090, so that at nine energies and five equations per energy, we had already used a vast amount of time. As we have said, we feel quite confident that we have attained a requisite accuracy, but our present inability to carry out further checks provides the most serious weakness in the present calculation. We hope to carry through some of these checks as bigger and faster computers become available.

We shall only include a few remarks concerning the numerical solution of the partial differential equations.[10] It is well known that if one uses a linear finite difference formula to represent the partial derivatives in a linear elliptic partial differential equation:

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+g(x,y)\varphi=f(x,y), \quad (3.1)$$

then the equation can be written as a matrix equation

$$\mathbf{A}\boldsymbol{\phi}=\mathbf{k}. \quad (3.2)$$

In the above $\mathbf{A}$ is an $N2\times N2$ matrix operating on the solution $\boldsymbol{\phi}$ at the $N2$ interior points. $\mathbf{k}$ is a column vector depending on the inhomogeneous term and the boundary values (assumed known). $N2$ being of the order of the square of the number of mesh points (N) along one boundary, a direct inversion of (3.2) is considered unattainable. It is for this reason that an iterative technique is usually employed.

In our own case it was found that various iterative techniques would not converge. We therefore utilized a direct inversion technique. The point is that although $\mathbf{A}$ is of gigantic dimension, it is of a special form and most of its elements are zero.

[10] Because of limitations of size and content the detailed description of this technique is not being included here. Nevertheless we feel that this method is of great importance to physicists as well as others faced with the problem of solving elliptic partial differential equation. The interested reader is referred to our NASA Technical Note D-1702 (unpublished).

TABLE III. Résumé of higher order results.

k (a.u.)	$\Delta\delta_0$ 0−10	$\Delta\delta_0$ 10−∞	$\Delta^2\delta_0^{(2)}$ 0−10	$\Delta^2\delta_0^{(2)}$ 10−∞	$\Delta^2\delta_0^{(1)}$ 0−10	$\Delta^2\delta_0^{(1)}$ 10−∞
0[a]	−0.20256	−0.3526	−0.012304	−0.00322	−0.001032	−0.00822
0.1	0.01895	0.01049	0.001168	0.000199	0.000369	0.000129
0.2	0.03136	0.00510	0.002016	0.000119	−0.000325	−0.000052
0.3	0.03530	0.00166	0.002418	0.000029	−0.00132	−0.000021
0.4	0.03373	0.00159	0.0024685	0.000026	−0.00228	+0.000019
0.5	0.03129	0.00188	0.002384	0.000041	−0.00140	0.0000049
0.6	0.02939	0.00131	0.002263	0.000028	−0.00141	−0.00000875
0.7	0.02766	0.00085	0.002145	0.000015	−0.00132	−0.0000003
0.8	0.02605	0.00096	0.002047	0.000019	−0.00130	−0.0000045

[a] For the purposes of the scattering length, the $k=0$ entries are negative.

In particular, in our own equations the matrix **A** can be written in diagonal form with elements which are themselves matrices. The diagonal elements are square matrices. Using some matrix manipulation, and known properties of tridiagonal matrices,[11] one of us (E. S.) has succeeded in reducing the problem to the sequential inversion of matrices of the same dimension and trivially related to these diagonal "elements." Thus the direct inversion of (3.2) in our case involves the inversion of matrices varying from 99×99 to 1×1 in size. This could be readily handled on our computing machine.

IV. RESULTS AND DISCUSSION

In Table III we have tabulated our results for the higher order corrections. The formula for $\Delta\delta_0$ has been given in the previous section. The remaining two integrals are

$$\Delta^2\delta_0^{(2)}=-\frac{2}{k\sqrt{5}}\left\{\int_0^R\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_2^{(0)}dr_1dr_2+\int_R^\infty\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_2^{(0)}dr_1dr_2\right\},\quad\text{(I5.8)}$$

$$\Delta^2\delta_1^{(1)}=-\frac{2}{k\sqrt{3}}\left\{\int_0^R\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_1^{(1)}dr_1dr_2+\int_R^\infty\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_1^{(1)}dr_1dr_2\right\}.\quad\text{(I5.9)}$$

The significance of the breakup of the integrals at $R=10$ has also been explained. In this connection it can hardly be overstressed that for small k a significant contribution comes from the region $R\leq r_1\leq\infty$.

In Table IV we have collected results to show the convergence of the terms multiplying successive powers of λ in the nonadabiatic series [cf. I equation (5.6)]. The convergence appears to be even more rapid than an order of magnitude per power of λ. In second order this is due to a partial cancellation of the terms multiplying λ^2, a circumstance which may very well have an increasingly important effect for high powers of λ due to the increasing number of terms which enter. (It is also possible that it might have the opposite effect.) The final δ in each row is then the sum of the entries to its left to the accuracy that we believe it is meaningful. As a simple extrapolation of the convergence, we take this to mean an uncertainty of 5 units in the last figure given for the phase shifts. (The scattering length will be discussed below.)

It must be reemphasized that this (λ) series is not identical to the more traditional series strictly in powers of l. The latter may be thought of as derived by truncating the original set of Eqs. [cf. I Eq. (2.4)] after $l=L$; i.e.,

$$\left[\Delta_{12}-l(l+1)(r_1^{-2}+r_2^{-2})+\frac{2}{r_1}+\frac{2}{r_2}-M_{ll}\right]\Phi_l=\sum_{m=0}^{L}M_{lm}\Phi_m,\quad l=0,1,\cdots,L.\quad(4.1)$$

Assuming that one could solve each of these problems exactly, one would obtain a sequence of phase shifts $\delta_{(L)}$ which would approach the exact phase shift:

$$\lim_{L\to\infty}\delta_{(L)}=\delta.$$

$\delta_{(0)}$ is of course our δ_0. Beyond that, Schwartz[12] has recently used his variational technique to solve for $\delta_{(1)}$.

TABLE IV. The convergence of the nonadiabatic series.

k (a.u.)	λ^0 δ_0	λ $\Delta\delta_0$	λ^2 $\Delta^2\delta_0^{(1)}+\Delta^2\delta_0^{(2)}$	δ
0	2.3482	−0.55516	−0.02477	1.7683
0.1	2.907728	0.02944	0.001865	2.9390
0.2	2.67942	0.03646	0.001758	2.7176
0.3	2.46158	0.03695	0.00111	2.4996
0.4	2.25800	0.03532	0.000235	2.2936
0.5	2.07102	0.03317	0.00104	2.1052
0.6	1.90189	0.03070	0.000872	1.9335
0.7	1.75070	0.02853	0.00084	1.7801
0.8	1.61666	0.02701	0.00076	1.6444

[11] A. S. Householder, in The University of Michigan Engineering Summer conferences, Numerical Analysis, No. 6207, 1962 (unpublished)

[12] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

TABLE V. Comparison of Schwartz's and nonadiabatic results.

k (a.u.)	Schwartz $\Delta\delta$	Non-adia-batic $\Delta\delta_0+\Delta^2\delta_0^{(1)}$	Schwartz $\sum_{i=2}^{\infty}\Delta^{(i)}\delta$	Non-adia-batic $\Delta^2\delta_0^{(2)}$	Schwartz δ	Non-adia-batic δ
0	0.5670	0.5644	0.0126	0.01552	1.7686	1.7683
0.1		0.02986		0.001367	2.9388	2.9390
0.2	0.0362	0.03608	0.0015	0.002135	2.7171	2.7176
0.3		0.03561		0.002447	2.4996	2.4996
0.4	0.0340	0.03306	0.0018	0.002495	2.2938	2.2936
0.5		0.03178		0.002425	2.1046	2.1052
0.6	0.0302	0.03038	0.0008	0.002291	1.9329	1.9335
0.7		0.02721		0.002160	1.7797	1.7801
0.8	0.0250	0.02571	0.0017	0.002066	1.643	1.6444

There is, however, a somewhat more fundamental, albeit more idealized, sequence $\delta_{(L)}$ which can be defined. Assume one had the exact wave function $\Psi(r_1,r_2,\theta_{12})$. Then one could obtain the exact $\Phi_l(r_1r_2)$ by suitably projecting $P_l(\cos\theta_{12})$ on Ψ. One could then obtain a sequence of $\delta_{(L)}$ from the basic relation

$$\sin(\delta-\delta_0)=-\frac{1}{k}\sum_{l=1}^{L}\frac{2}{(2l+1)^{1/2}}\times\int\int\Phi_0^{(0)}\frac{r_2{}^l}{r_1{}^{l+1}}\Phi_l dr_1dr_2. \quad \text{(I3.5)}$$

Clearly the second of these sequences of $\delta_{(L)}$ cannot be worse than the first (although the first obviously comes from a variational principle).

In Table V we have collated the results of Schwartz's and our calculations which bear on the latter sequence of $\delta_{(L)}$. The column marked $\Delta\delta$ is the difference $\delta_{(1)}-\delta_0$ in Schwartz's calculation.[13] The approximation here is the neglect of the back coupling of the higher Φ_l which distinguishes between the first and the second sequences of $\delta_{(L)}$. The analog of $\Delta\delta$ in our case is $\Delta^2\delta_0+\Delta^2\delta_0^{(1)}$. Here the back coupling is consistently taken into account, but we have only included two terms of a (presumably rapidly convergent) infinite series. In the column marked $\Delta^2\delta_0^{(2)}$ we have presented only the first term of the relevant infinite series. The corresponding column of Schwartz has been obtained by subtracting his final phase shifts from $\delta_{(1)}$. If his ansatz for the wave function were exact, one could conclude that this was the contribution of all remaining multipoles,

$$\sum_{i=2}^{\infty}\Delta^{(i)}\delta.$$

However the ansatz for the complete wave function contains (presumably) about the same number of parameters as that used in obtaining $\delta_{(1)}$. Therefore it is by no means clear that projecting out Φ_1 from his Ψ will give the same accuracy as his explicitly calculated $\delta_{(1)}$.

[13] Some time ago we requested Dr. Schwartz to utilize his Hylleraas variational approach to calculate δ_0 by omitting all terms depending on r_{12}. Dr. Schwartz kindly carried out these calculations which served as a check on our original zeroth-order results (reference 2). The calculations were subsequently expanded to comprise the contents of Tables II and III of reference 12.

For these reasons it can hardly be expected that there would be equality between the corresponding entries in Table V. Nevertheless the rather wide deviation of the individual entries bespeaks of the possibility that the agreement to almost 5 significant figures in the final phase shifts may be somewhat coincidental. For the purposes of later discussion it should be noted that our quadrupole contribution is larger than all the remaining multipoles in Schwartz's calculation. (Thus his results suggest a more rapid rate of convergence of the l expansion than our own!)

Schwartz has also commented[12] on the relative angular momentum expansion in these types of problems. (The part of his scattering calculation which concerns the triplet phase shift has been given in Table V.) The bulk of his calculation is concerned with the second order energy (for the singlet spin state):

$$E_2=\left(\sum_n+\int dn\right)\frac{|\langle 0|2/r_{12}|n\rangle|^2}{E_0-E_n}. \quad (4.2)$$

Using the well-known expansion of $2/r_{12}$ in Legendre polynomials,

$$\frac{2}{r_{12}}=2\sum_{l=0}^{\infty}\frac{r_<{}^l}{r_>{}^{l+1}}P_l(\cos\theta_{12}),$$

he can put (4.2) into the form

$$E_2=\sum_{l=0}^{\infty}E_2(l), \quad (4.3)$$

where the $E_2(l)$ can be well defined.[14] With each $E_2(l)$ there is associated a wave function $\Psi_1(l)$ which, aside from the angular dependence $P_l(\cos\theta_{12})$, is a function of the two radial variable r_1 and r_2. Reduced to its bare essentials, Schwartz's argument runs as follows: if one treats each l problem variationally with the usual type of smooth polynomial trial functions, then the $l=0$ and $l=1$ problems can be well approximated whereas the higher l problems become increasingly difficult. The reasons for the increasing difficulty of approximation by conventional means is due to the fact that the functions $\Psi_1(l)$ have discontinuities in their second derivates coming ultimately from different analytic forms of $r_<{}^l/r_>{}^{l+1}$ in the regions $r_1>r_2$ and $r_1<r_2$. The discontinuities correspond to the $\Psi_1(l)$ becoming more and more sharply peaked about the line $r_1=r_2$. On the basis that the bump itself provides the dominant contribution to the energy, Schwartz has derived the asymptotic formula for large l

$$E_2(l)\cong-(45/256)(1/l^4). \quad (4.4)$$

This then, defines, the convergence of this specific problem, rather than any inaccurate calculations for

[14] C. Schwartz, *Methods in Computational Physics* edited by B. Alder, S. Fernbach, and M. Rotenberg [Academic Press Inc., New York (to be published)].

$E_2(l)$ for $l>1$, which in general will tend to give the idea of a much more rapid convergence.[15]

Formula (4.4) applies to the specific problem of the second-order energy in the singlet (space-symmetric) state, however it is not unreasonable to assume l^{-n} characterizes the complete energy (or other physical property) in the l expansion. Whether l^{-n} constitutes a rapidly convergent series depends on the type of problem with which one is dealing. In bound state problems where much greater experimental accuracy is in general available, one must be quite demanding in this regard. Even here, however, the convergence of (4.4) is not in principle uncompetitive with traditional techniques. Thus if one associates the inclusion of an additional l component with the inclusion of an additional parameter in conventional expansions, in which the use of 100 and[6] even 1000 parameters[16] has now been accomplished, one would get a competitive 8 to 12 significant figure accuracy. The fact that one cannot use a (presently) conventional approach in accomplishing this, is not an *a priori* objection to the rate of convergence of the l expansion.

In his discussion of the extension of the relative partial wave treatment to the scattering problem, we find that Schwartz has insufficiently stressed the different physics involved. First it is clear that because of the disparity in experimental accuracy one does not need anything like the accuracy of a bound state problem to correlate theory with experiment.

In order further to discuss the scattering case, it is necessary to clear up some points. In scattering calculations r_1r_2 times the wave function has a nonvanishing component:

$$\lim_{r_1\to\infty} r_1r_2\Psi = A\sin(kr_1+\delta)R_{1s}(r_2),$$

which must be included in order to make any kind of analysis. In discussing the aspects of $r_1r_2\Psi$ below, we shall always disregard this nonvanishing component.

The main difference between the bound state wave function (with any kind of forces) and scattering wave functions (involving Coulomb forces) is that the bound state wave function vanishes exponentially in all asymptotic regions of configuration space whereas the scattering wave function does not. It has been one of the primary points of the nonadiabatic theory in the decomposition of $r_1r_2\Psi$ in terms of $P_l(\cos\theta_{12})$, (I2.3), that the associated Φ_l can be shown to have slowly vanishing adiabatic forms

$$\lim_{r_1\to\infty}\Phi_l \sim -\frac{2}{(2l+1)^{1/2}}\frac{\sin(kr_1+\delta)}{r_1^{l+1}}e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right).$$

It has further been derived as one of the main results of this theory that the scattering length due to the dipole term will be diminished by an amount

$$a=a(R)-\frac{9}{2}\left(\frac{1}{R}-\frac{a+a_0}{2R^2}+\cdots\right),$$

where $a(R)$ comes from a wave function which is more sharply cut off and hence more characteristic of a problem in a finite "sphere" of radius R. This prediction[17] was tacitly confirmed by the calculation of Schwartz[5] in which, when the variational counterpart of Φ_1 was included, his scattering length was reduced by over 5%. Thus, whereas the nonadiabatic theory incorporates both short-range correlations (via the convergent expansion in l) and long range effects naturally, the Hylleraas type wave function by itself cannot practically deal with the latter. [Tables II and III of Schwartz's paper[12] include Φ_1 in the calculations of the $k=0$ entries for $\lambda(s+p)$ as well as λ (complete).]

That a Hylleraas-type wave function does not naturally describe the long-range correlations can be further brought home by reference to the paper of Ohmura and Ohmura.[18] In their deduction of the singlet scattering length, these authors required the coefficient $C(\infty)$ in the adiabatic form

$$\lim_{r_1\to\infty}\Psi = C(\infty)\frac{e^{-\gamma r_1}}{r_1}\frac{R_{1s}(r_2)}{r_2} \qquad (4.4)$$

of the H^- wave function. Here γ is the square root of the electron affinity and being small it makes the term simulate the nonvanishing term in a scattering calculation. This form is not the analytic form of the Pekeris or Hylleraas wave functions both of which have the exponential dependence

$$\exp[-\tfrac{1}{2}|E|^{1/2}(r_1+r_2)],$$

where E is the total energy of the H^- ion. In order to evaluate $C(\infty)$, Ohmura and Ohmura used the 161 and 203 parameter Pekeris wave functions.[6] They concluded that, whereas the wave function reproduces the adiabatic form (4.4) quite accurately in the region $r_1=10$

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[15] Reference 12 must be read very carefully here; otherwise it may give the erroneous impression that

$$\sum_{l=2}^{4} E_2(l) \cong (2/3)\sum_{l=2}^{\infty} E_2(l)$$

which, if it were true, would be a more serious criticism of the convergence. What, in fact, is being asserted is that Schwartz's conventional calculation of

$$\sum_{l=2}^{4} E_2(l)$$

must be in error in such a way as to give a spurious rate of convergence. Nevertheless one can be quite sure that the correct

$$\sum_{l=2}^{4} E_2(l) \gtrsim (0.99)\sum_{l=2}^{\infty} E_2(l).$$

[16] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[17] A. Temkin, private communication to C. Schwartz.

[18] T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960).

~ 12 ($r_2=0$), deviations in the variational approximations for $r_1 \geq 12$ were quite noticeable.

We shall now show that the inability of Schwartz's zero-energy wave function to describe the adiabatic part of the quadrupole term can explain the difference between his triplet scattering length 1.7686 (in units of Bohr radii), and our own, 1.7683. To repeat, at zero energy Schwartz's Ψ is made to contain $\Phi_1^{(\text{adiab})}$ but not $\Phi_2^{(\text{adiab})}$. Using the same type analysis that we made on the dipole effect, we can write the long-range contribution of the quadrupole term as

$$a(R)-a=\lim_{k\to 0 k2}\frac{2}{\sqrt{5}}\int_R^\infty\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_2 dr_1 dr_2$$

$$\cong\left[\frac{15}{k^2}\int_R^\infty\frac{\sin(kr+\delta_0)\sin(kr+\delta)dr}{r^6}\right]_{k\to 0}$$

$$\cong 15\left(\frac{1}{3R^3}-\frac{1}{4}\frac{(a+a_0)}{R^4}+\cdots\right).$$

If we associate Schwartz's value with $a(R)$, a very reasonable choice of R ($R\cong 25$) will reproduce our own value for a. Although from the experimental point of view the difference between the two numbers is completely negligible, it is worth noting that the new scattering length is outside of Schwartz's limit of error.[5] We are inclined to think that the unaccounted for higher multipole may subtract an additional unit in the fourth significant figure (cf. the $k=0$ row of Table IV). We would extrapolate the triplet scattering length to be (in units of Bohr radii)

$$a_t=1.767.$$

A question remains at nonzero energies as to the effect of the slowly vanishing multipoles. The answer obviously depends on the accuracy in question. Schwartz finds[5] that the effects are "washed out" to his accuracy whereas our own calculation suggests that particularly the dipole contribution is not negligible. It may very well be that our inclusion of these effects as opposed to Schwartz's inclusion of the higher multipoles balance each other out, and that both calculations give lower bounds for the phase shifts.

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