

less sensitive on the lower limit and the "classical" method of calculating ΔE as the difference between the $1s\sigma_g$ and the $2p\sigma_u$ potential curves is a much better approximation. It was the one used in the computation. Numerical checks showed the error to be less than 1% at $V_0=0.6$ and then to increase slowly as V_0 was made smaller. The method of summing simultaneous excitations made use of the approximate formula given in Eq. (21). The appropriate correction term for the continuum was evaluated according to Eq. (22) and then added to the results from the approximate summation formula.

Comparison of the results that include simultaneous excitation with Fig. 3, which shows the cross section when these events are ignored, demonstrates their importance. It is apparent that the first Born approximation must include these processes when it is possible for them to occur. This is especially significant since their influence is the strongest at the high energies where the Born approximation is most likely to be used. As yet

there is no experimental evidence to compare with these results, but the influence of simultaneous excitations on the dependence of the cross section is suggestive when one looks at the results obtained for the H_2^+ , H_2 scattering system.¹⁷

ACKNOWLEDGMENT

The author wishes to express his gratitude to Thomas A. Green and Gordon W. McClure for many helpful discussions which contributed significantly to the scope of this paper and to Mrs. Marcella Madsen for writing the digital computer programs required by this work and for aid in the numerical analysis.

The author also wishes to thank Victor Brady and the Lawrence Radiation Laboratory of the University of California for their generosity in providing a magnetic tape containing the hydrogen molecule-ion ground-state vibrational wave functions.

¹⁷ J. Guidini, *Compt. Rend.* **253**, 829 (1961).

Minimum-Principle Calculation of the Positron-Hydrogen *s*-Wave Phase Shift*

YUKAP HAHN AND LARRY SPRUCH

Physics Department, New York University, Washington Square, New York, New York

(Received 16 April 1965)

The recently developed improved minimum principle for single-channel scattering is applied to a study of the *s*-wave elastic-scattering phase shift η_0 of positrons by atomic hydrogen. The method requires the exact solution of the static one-body equation and of the corresponding static Green's function, and also the orthogonalization of the trial function to the hydrogenic ground-state wave function. The radial part of the trial function $Q\Psi_l$ is chosen to be of the exponential-polynomial form, with linear and nonlinear variational parameters; to simplify the orthogonalization, $Q\Psi_l$ is expanded in Legendre polynomials whose argument is the cosine of the angle between the coordinate vectors of the electron and the positron. Rigorous lower bounds are obtained on η_0 at various energies. The calculation includes the contributions from hydrogenic states with angular momentum l up to $l=5$. For each energy, an estimate is made by extrapolation of the true contribution to η_0 from $0 \leq l \leq 5$, and this estimate is used in turn to estimate the contribution from $l > 5$ to η_0 . The rigorous lower bounds obtained and the estimates are compared with previous estimates of η_0 .

I. INTRODUCTION

A LARGE number of calculations have recently been performed of the scattering of electrons by atomic hydrogen, at low¹⁻⁴ and at high energies. This is on the one hand a reflection of the increased interest in atomic scattering processes in the atmosphere of the earth and of the sun, for example, and on the other hand of the presence of high-speed computers which make

possible large-scale calculations aiming at high accuracy. In view of the concurrent recent interest of the experimentalists and of the consequent improvements in technique, there is little doubt that relatively precise contact will be made shortly between the experimental results and theoretical calculations based on first principles, even for energies at which the distortion of the hydrogen atom is great enough to more or less completely invalidate the Born approximation. We might remark parenthetically that, roughly speaking, such contact has just about been made for scattering by an atom. It would obviously be extremely useful to the experimentalist to be able to normalize cross-section data by the use of reliable theoretical results.

Because of the great similarity of the problems, in the course of studying e^-H scattering the theorists have

* The research reported on in this article was sponsored by the U. S. Office of Naval Research, and the Advanced Research Projects Agency under Contract Nonr-205 (49), NR 012-109, and NASA under Contract No. NSG 699.

¹ L. Rosenberg, L. Spruch, and T. F. O'Malley, *Phys. Rev.* **119**, 164 (1960).

² C. Schwartz, *Phys. Rev.* **124**, 1468 (1961).

³ A. Temkin, *Phys. Rev.* **126**, 130 (1962).

⁴ P. G. Burke and K. Smith, *Rev. Mod. Phys.* **34**, 458 (1962).

naturally tended simultaneously to consider e^+H scattering.^{2,5-8} The formal setting up of the e^+H scattering problem is simpler because the Pauli principle does not enter, but at least at very low energies this simplicity is largely offset from a calculational point of view because of the tremendous distortion that the positron produces, presumably through the virtual formation of positronium⁵ in its ground state and in excited states. At zero energy, for example, it was rigorously proven⁵ that contrary to simple expectations and to previous calculations, the scattering length is negative, reflecting an effective attraction between the positron and the hydrogen atom.

The rigorous result just referred to was one of a number of zero-energy calculations in atomic^{1,5} and nuclear scattering problems^{9,10} based on a minimum principle which provides a bound on the scattering length.^{9,11} The extension of the minimum principle to nonzero energies was only recently derived in a really usable form,^{12,13} and the present positron-atomic-hydrogen calculation, restricted to the case of zero total angular momentum, represents the first serious application^{14,15} of the method.

II. THE MINIMUM PRINCIPLE

We here consider only the single-channel scattering of positrons by hydrogen atoms, and we are

therefore restricted to incident energies E' less than 6.8 eV, the energy at which pickup becomes possible. Neglecting the possibility of annihilation we choose as our Hamiltonian

$$H = -(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) - e^2/r_1 + e^2/r_2 - e^2/r_{12}, \quad (2.1)$$

where \mathbf{r}_1 and \mathbf{r}_2 represent the electron and positron coordinates, respectively. The present paper will be concerned only with zero orbital angular momentum scattering and the wave function Ψ will therefore be independent of the Eulerian angles. Two standard choices of the three remaining coordinates include r_1, r_2, r_{12} and r_1, r_2, θ_{12} , where θ_{12} is the angle between \mathbf{r}_1 and \mathbf{r}_2 . Each choice has its advantages, but we chose the second set for two reasons. Firstly, we require the trial function $Q\Psi_l$ to be orthogonal to the hydrogenic ground-state wave function $\psi_{T0}(r_1)$, and it is somewhat simpler, although *not* essential, to choose such a trial function if one uses r_1, r_2, θ_{12} coordinates. Secondly, with this choice it is somewhat simpler to generalize to higher partial waves.¹⁵

Our problem is to determine the zero angular momentum phase shift, η_0 , defined by the solution of the equation,

$$\left\{ \frac{\hbar^2}{2m} \left[-\frac{\partial^2}{\partial r_1^2} - \frac{\partial^2}{\partial r_2^2} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin\theta_{12}} \frac{\partial}{\partial \theta_{12}} \sin\theta_{12} \frac{\partial}{\partial \theta_{12}} \right] - \frac{e^2}{r_1} + \frac{e^2}{r_2} - \frac{e^2}{r_{12}} - E \right\} \{r_1 r_2 \Psi(r_1, r_2, \theta_{12})\} = 0, \quad (2.2)$$

where Ψ is regular at the origin and has the asymptotic behavior

$$\Psi \rightarrow \psi_{T0}(r_1) \sin(kr_2 + \eta_0) / [r_2 \sin(\eta_0 - \theta)], \quad r_2 \rightarrow \infty. \quad (2.3)$$

⁵ L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960).

⁶ M. Rotenberg, Ann. Phys. (N. Y.) **19**, 262 (1962).

⁷ R. S. Ruffine, New York University Research Report No. CX-48 (unpublished).

⁸ A. Temkin, Proc. Phys. Soc. (London) **A80**, 1277 (1962); also private communication.

⁹ L. Spruch and L. Rosenberg, Phys. Rev. **117**, 1095 (1960).

¹⁰ L. Spruch and L. Rosenberg, Nucl. Phys. **17**, 30 (1960); Kalikstein, Rosenberg, and Spruch, *ibid.* **49**, 257 (1963); L. M. Delves, J. N. Lyness, and J. M. Blatt, Phys. Rev. Letters **12**, 542 (1964). See also L. Spruch, in *Ninth Yugoslav Summer School in Nuclear Physics Hercegovi, 1964*, edited by M. Cerineo (Yugoslavian Atomic Energy Commission, Belgrade, to be published).

¹¹ L. Spruch and L. Rosenberg, Phys. Rev. **116**, 1034 (1959); L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **118**, 184 (1960).

¹² Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **130**, 381 (1963).

¹³ L. Rosenberg and L. Spruch, Phys. Rev. **121**, 1720 (1961), derived a variational bound for nonzero energies, but the requirement that certain potentials be truncated complicates the method.

¹⁴ Preliminary results for $L=0$ e^+H were reported on by Y. Hahn, T. F. O'Malley, and L. Spruch, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions, London, 1963*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 312. The trial function used was somewhat crude and the contributions

The constant θ , which satisfies $0 \leq \theta < \pi$ but is otherwise arbitrary, will be chosen later. The total energy of the system E is given by

$$E = E_{T0} + E' = -13.6 \text{ eV} + \hbar^2 k^2 / 2m,$$

while the ground-state wave function $\psi_{T0}(r_1)$ is normalized by

$$\int \psi_{T0}^2(r_1) r_1^2 dr_1 = 1.$$

The projection operator P that appears in the non-zero energy minimum-principle formulation¹² is here taken to be that which projects on to the ground state of the hydrogen target. Without loss of generality, we can include in P the projection on to the $P_0(\cos\theta_{12})$ state as well, since then the components of $Q\Psi_l$ which are proportional to P_l for $l \neq 0$ are already orthogonal to

for $l \geq 5$ were underestimated; this had the further effect of causing the estimates of the contribution from $l > 5$, obtained by extrapolation, to be greatly underestimated.

¹⁵ The p -wave and d -wave phase shifts for e^+H scattering have been calculated by the techniques of the present paper by C. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. (to be published); and adiabatic and variational calculation have been performed by R. J. Drachman, Phys. Rev. **138**, A1582 (1965), and by R. L. Armstead and C. Schwartz (unpublished), respectively.

$\psi_{T_0}(\mathbf{r}_1)P_0$ without adjusting the radial parts of the function. In fact, the choice of the coordinates made above readily allows the construction of $Q=1-P$. We thus define, for an arbitrary function $f(\mathbf{r}_1, \mathbf{r}_2, \theta_{12})$,

$$Pf(\mathbf{r}_1, \mathbf{r}_2, \theta_{12}) = \frac{1}{2}\psi_{T_0}(\mathbf{r}_1) \times \int \psi_{T_0}(\mathbf{r}_1') f(\mathbf{r}_1', \mathbf{r}_2, \theta_{12}') r_1'^2 d\mathbf{r}_1' d\cos\theta_{1'2}, \quad (2.4)$$

where the $\frac{1}{2}$ arises because of the integration over $d\cos\theta_{1'2}$, and the equation in the static approximation by

$$P(H-E)P\Psi^P=0 \quad (2.5)$$

with

$$P\Psi^P = \psi_{T_0}(\mathbf{r}_1)u_0^P(\mathbf{r}_2)/r_2. \quad (2.6)$$

($\theta_{1'2}$ is a dummy variable and need not therefore be given a physical interpretation, but it can be interpreted in the six-dimensional space defined by \mathbf{r}_1' and \mathbf{r}_2 as the angle between these vectors. In the present case where we are dealing with $L=0$, Pf is actually independent of $\theta_{1'2}$.) Explicitly, we have

$$[-d^2/dr_2^2 + V_{00}(\mathbf{r}_2) - k^2]u_0^P(\mathbf{r}_2) = 0, \quad (2.7)$$

where

$$V_{00}(\mathbf{r}_2) = (2/a_0)e^{-2r_2/a_0}[(1/a_0) + (1/r_2)] \quad (2.8)$$

is $2m/\hbar^2$ times the potential in the static approximation, and where $u_0^P(\mathbf{r}_2)$ satisfies the boundary conditions $u_0^P(0) = 0$

$$u_0^P(\mathbf{r}_2) \rightarrow \sin(kr_2 + \eta_0^P)/\sin(\eta_0^P - \theta), \quad r_2 \rightarrow \infty. \quad (2.9)$$

The determination of the static phase shift η_0^P is therefore a completely trivial matter with the use of a computer.

Our basic inequality¹² is

$$ka_0 \cot(\eta_0 - \theta) \leq ka_0 \cot(\eta_0^P - \theta) + \Delta_\theta \equiv ka_0 \cot[\eta_0(MP) - \theta], \quad (2.10)$$

where

$$(\hbar^2/2ma_0)\Delta_\theta = 2(Q\Psi_t, QHP\Psi^P) + (Q\Psi_t, Q[H+HG^PH-E]Q\Psi_t). \quad (2.11)$$

With a_0 the Bohr radius, we choose $Q\Psi_t$ to be of the form

$$Q\Psi_t = \sum_{l,i} c_{li} \chi_{li}(\mathbf{r}_1/a_0) \times \omega_{li}(\mathbf{r}_2/a_0) P_l(\cos\theta_{12}) / (r_1 r_2 a_0^{1/2}) \quad (2.12)$$

with

$$\chi_{li}(x_1) = x_1^{l+1} \exp(-b_{li}x_1) - x_1(2/(1+b_{0i}))^2 [\exp(-x_1)] \delta_{0l} \quad (2.13)$$

and

$$\omega_{li}(x_2) = x_2^{l+1} \exp(-d_{li}x_2), \quad (2.14)$$

where $x_i = \mathbf{r}_i/a_0$ and δ_{0l} is the Kronecker delta function. The distinction between $l=0$ and $l \neq 0$ in the form for $\chi_{li}(\mathbf{r}_1)$ is a consequence of the fact that for $l \neq 0$ the

orthogonality to $\psi_{T_0}(\mathbf{r}_1)$ is automatically accomplished by the presence of the $P_l(\cos\theta_{12})$, while for $l=0$ one must choose the radial function $\chi_{0i}(\mathbf{r}_1)$ to be orthogonal to $\psi_{T_0}(\mathbf{r}_1)$.

The validity of the inequality (2.10) presupposes that $Q\Psi_t$ contains all states which give a negative expectation value of the operator $Q[H+HG^PH-E]Q$, that is, that no more subtraction terms are necessary. There could be very few such states, if any, and our $Q\Psi_t$ will contain enough terms so that the validity of the inequality is effectively guaranteed. The monotonic decrease of the estimate of $ka_0 \cot(\eta_0 - \theta)$ serves as a partial check on the validity of the bound. Thus, while we cannot formally prove the rigor of the bound without an elaborate calculation, and while a certain degree of caution is always necessary, there can be very little question that we do in fact have a bound and that the calculational procedure has all of the advantages associated with a formal rigorous bound.

The Green's function G^P satisfies the equation

$$P(H-E)PG^P = -P \quad (2.15)$$

and thus is factorizable, that is, we have

$$G^P(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \psi_{T_0}(\mathbf{r}_1) \psi_{T_0}(\mathbf{r}_1') g^P(\mathbf{r}_2, \mathbf{r}_2') \quad (2.16)$$

with g^P satisfying the equation

$$(\hbar^2/2m)[- (d^2/dr_2^2) + V_{00}(\mathbf{r}_2) - k^2] \times \{g^P(\mathbf{r}_2, \mathbf{r}_2') r_2 r_2'\} = -\delta(\mathbf{r}_2 - \mathbf{r}_2').$$

Since $V_{00}(\mathbf{r}_2)$ is local, $g^P(\mathbf{r}_2, \mathbf{r}_2')$ can be given in the form

$$(\hbar^2/2m)g^P(\mathbf{r}_2, \mathbf{r}_2') = -(1/kr_2 r_2') [u_0^P(\mathbf{r}_<) v_0^P(\mathbf{r}_>) - \frac{1}{2} \sin(2\eta_0^P - 2\theta) u_0^P(\mathbf{r}_<) u_0^P(\mathbf{r}_>)], \quad (2.17)$$

where the irregular function $v_0^P(\mathbf{r})$ satisfies the same equation as does $u_0^P(\mathbf{r})$, that is, Eq. (2.7), and satisfies the boundary condition

$$v_0^P(\mathbf{r}_2) \rightarrow \sin(\eta_0^P - \theta) \cos(kr_2 + \eta_0^P), \quad (2.18)$$

where $\mathbf{r}_<$ and $\mathbf{r}_>$ are the smaller and the larger, respectively, of \mathbf{r}_2 and \mathbf{r}_2' . g^P as given by (2.17) assumes the correct asymptotic form required for the difference between $P\Psi$ and $P\Psi^P$ with the asymptotic boundary conditions given by (2.3) and (2.9), respectively.

For a set of suitably chosen nonlinear parameters b_{li} and d_{li} in the trial function $Q\Psi_t$ of Eq. (2.12), minimization of Δ_θ of (2.11) can be carried out trivially with respect to variations of the linear parameters c_{li} . Denoting the double sum in l and i by a single sum in p , we have

$$\Delta_\theta = 2 \sum_p c_p N_p + \sum_{p,q} c_p K_{pq} c_q \equiv 2C \cdot N + C \cdot KC, \quad (2.19)$$

where N_p and K_{pq} are the elements defined in Appendix

C. Δ_θ assumes its minimum value

$$\Delta_\theta = -N \cdot K^{-1}N \quad (2.20)$$

for

$$C = -K^{-1}N, \quad (2.21)$$

and is independent of normalization since $Q\Psi_i$ appears quadratically in K and only linearly in N .

We now consider the choice of the normalization constant θ . If θ is chosen such that the inequality $\eta_0^P < \theta < \eta_0$ holds, then we have a subtraction term on the right hand side of (2.11), but a sufficiently accurate wave function could easily take into account this subtraction term. However, for θ chosen outside the range given above, this spurious subtraction is not necessary. Therefore, we have made the particular choice in all of our subsequent calculations

$$\theta = \frac{1}{2}\pi + \eta_0^P, \quad (2.22)$$

for which in the present problem it is almost certain that $\eta_0 < \theta$. This choice of θ reduces the inequality (2.10) to the simple form

$$ka_0 \tan(\eta_0 - \eta_0^P) \geq -\Delta_{\frac{1}{2}\pi + \eta_0^P} \geq 0. \quad (2.23)$$

$\Delta_{\frac{1}{2}\pi + \eta_0^P}$ will be written from now on simply as Δ .

III. RESULTS OF THE CALCULATION

A. Close Coupling Approximation

If a few eigenstates of the hydrogen atom are chosen for $\chi_{li}(r_1)$ in (2.12), the exact phase shifts are sometimes available from the close coupling approximation (c.c.a.) calculations. These c.c.a. results have previously been shown to provide bounds on the true phase shift.¹⁶ In order to check our program and also to obtain indications as to how easily the minimum principle can reproduce the known results, we have calculated the phase shifts for a few cases for which $Q\Psi_i$ contains one or more excited states of the hydrogen atom with principal quantum number n and orbital angular momentum $l = n - 1$, that is $2p, 3d, 4f$, etc. These states can be put in trivially by simply setting $b_{li} = n^{-1}$ in the trial function (2.12); the form (2.13) cannot, as it stands, handle the eigenstates with $n \neq l + 1$ since they contain polynomials in r_1 which are not of that form.

We compare our result with those obtained from the exact numerical solution of the coupled equations derived in the close coupling approximations.^{17,18} As shown in Table I, the agreement is satisfactory, although no attempt was made to optimize the choice of the nonlinear parameters d_{li} ; we simply chose $d_{li} = d_{li-1} + (0.1)i$ for $i = 1, 2, \dots, 9$ and $d_{l0} = 0.2$. Note that the phase shifts obtained by the minimum principle (MP) are in each

¹⁶ Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

¹⁷ P. G. Burke and K. Smith, Ref. 4 and private communication.

¹⁸ P. A. Fraser and R. P. McEachran (private communication). The calculations were based on the same code that was used in their article in Proc. Phys. Soc. (to be published).

TABLE I. Phase shifts obtained for the close coupling approximation (c.c.a.) in which the target can only be in its ground state or in certain specified excited states. The numerical (numer.) results were obtained by "exact" numerical solution of the coupled differential equations that arise in the c.c.a. The numerical results quoted are those of P. A. Fraser and R. P. McEachran^a and are lower in each case than the values obtained by P. G. Burke and K. Smith^b by two units in the last digit. The minimum principle (MP) results for the given c.c.a. are those of the present paper.

States	Method	$ka_0=0.2$	$ka_0=0.4$	$ka_0=0.6$
1s	Numer.	-0.1145	-0.2181	-0.3042
1s+2p	Numer.	-0.0458	-0.1531	-0.2547
	MP	-0.0458	-0.1532	-0.2550
1s+3d	Numer.		-0.2175	
	MP		-0.2175	
1s+2p+3d	Numer.	-0.0433	-0.1512	-0.2537
	MP	-0.0434	-0.1513	-0.2540

^a See Ref. 18.

^b See Ref. 17.

case either equal to or *lower* than the correct values, as they must be. It is also of interest to remark that the apparently rapid convergence of the phase shift as a function of l is completely misleading insofar as the final phase shift is concerned since the convergence in the principal quantum number n for a fixed l is extremely slow. This strongly suggests that the usual close coupling approximation, although it provides bounds,¹⁶ often converges very slowly as a function of the number of target eigenstates included. We might note that a MP calculation of a phase shift for a given c.c.a. provides a lower bound on the exact c.c.a. phase shift, and therefore on η itself, since the exact c.c.a. phase shift provides a lower bound on η .

B. A Rigorous Lower Bound on η_0 and an Estimate of η_0

For the (rather limited) form of the trial function that we have chosen, there occur two nonlinear parameters b_{li} and d_{li} for each linear parameter c_{li} . Searching procedures for nonlinear parameters as well as a variation in the form of trial function to test the long-range effect are described in Appendix A. Using the set of nonlinear parameters obtained by analyzing the effects of each l state separately, the linear parameters were re-determined by minimizing the full Δ , which includes

TABLE II. The phase shifts $\eta_0(l, MP)$ obtained by the minimum principle, in which virtual excitations to the target states with angular momenta up to and including l are allowed. These values are rigorous lower bounds. N_l gives the number of linear variational parameters used for the given l while Σ_l gives the total number used for states up to and including l .

l	$ka_0=0.2$	$ka_0=0.4$	$ka_0=0.6$	N_l	Σ_l
0	-0.1058	-0.2001	-0.2760	7	7
1	0.0612	-0.0160	-0.1114	12	19
2	0.1128	0.0416	-0.0607	10	29
3	0.1340	0.0652	-0.0406	9	38
4	0.1443	0.0763	-0.0316	8	46
5	0.1494	0.0818	-0.0272	7	53

TABLE III. The phase shifts $\tilde{\eta}_0(l)$ obtained by including the estimated correction due to the inaccuracy in the trial function, and the estimate $\tilde{\eta}_0(\infty)$ obtained by including the extrapolation contributions from $l > 5$. Neither the $\tilde{\eta}_0(l)$ nor $\tilde{\eta}_0(\infty)$ are rigorous lower bounds. The number in parentheses represents our estimate, based on our own calculations, of the error in the last figure.

l	$ka_0=0.2$	$ka_0=0.4$	$ka_0=0.6$
0	-0.105(0)	-0.200(0)	-0.275(0)
1	0.064(1)	-0.012(1)	-0.107(1)
2	0.118(2)	0.049(2)	-0.053(3)
3	0.142(3)	0.076(4)	-0.029(4)
4	0.154(3)	0.090(4)	-0.018(5)
5	0.161(5)	0.098(7)	-0.011(5)
∞	0.182(11)	0.119(13)	0.009(12)

coupling between states of different l . The resulting phase shifts $\eta_0(l, \text{MP})$, which include contributions from states of angular momenta up to and including l , with coupling effects accounted for, are given in Table II. They are the main results of this paper and represent *rigorous* lower bounds on the s -wave phase shifts for the fictitious problem in which the hydrogen atom is allowed to be virtually excited to states with arbitrary principal quantum numbers but with angular momenta only up to and including l . They *also* provide rigorous bounds on the true phase shifts η_0 .

As noted previously the present choice of the coordinate system makes it trivial to satisfy the orthogonality requirement, but it has the well-known drawback that $\eta_0(l)$ as a function of l does not converge very rapidly. Furthermore, the component of the wave function with angular momentum l becomes increasingly difficult to obtain as l becomes large, presumably due to the singular interaction component of the form $r <^l / r >^{l+1}$. We have made first a crude estimate of the error in $\eta_0(l, \text{MP})$ due to the inaccurate trial function $Q\Psi_t$. The corrected estimate of the total contribution for states of angular momenta up to l is denoted by $\tilde{\eta}_0(l)$. We then extrapolated to $l > 5$ using the corrected values $\tilde{\eta}_0(l)$. Details of the correction and extrapolation procedures are given in Appendix B, while Table III contains the nonrigorous *estimated* phase shifts. Table IV compares

TABLE IV. Various estimates of the s -wave phase shift at $ka_0=0.2$. The values obtained by the MP give rigorous lower bounds.

Authors	all s	$1s + \text{all } p$	all $s + \text{all } p$	all states
Spruch-Rosenberg ^a	0.156
Ruffine ^b	...	0.045
Schwartz ^c	-0.105	0.188
Temkin ^d	0.056	...
Brandsen ^e	0.057
MP-rigorous	-0.106	0.052	0.061	0.149 ^f
MP-estimated	-0.105	0.054	0.064	0.182

^a See Ref. 5. An "almost MP calculation."

^b See Ref. 7. A self-consistent calculation.

^c See Ref. 2. An interesting variational calculation.

^d See Ref. 8. A nonadiabatic calculation.

^e See Ref. 19. A perturbation calculation.

^f This value is obtained by allowing virtual excitations only to states with $0 \leq l \leq 5$.

the various estimates^{2,5,7,8,19} of the s -wave shift at $ka_0=0.2$.

IV. DISCUSSION

We have obtained rigorous lower bounds on the phase shift, and have obtained estimates of the phase shift. The estimates were crude because of the difficulty in simulating the wave function for large l and also because of the slow convergence in l . Our calculation shows however several interesting features of the e^+H scattering problem. As expected the effect of the target distortion during the collision is very important, presumably due to the virtual formation of positronium. Thus the contribution from large l states seems to be dominated by the behavior of the wave function in the region $r_1 \approx r_2$. However, the wave function near this region is very difficult to calculate due to the singular behavior of the potential $-e^2/r_{12}$. This is in contrast to the e^-H scattering problem where the Pauli principle plays a major role and imposes stringent boundary conditions at $r_1=r_2$, and where the repulsive potential minimizes the importance of the region $r_1 \approx r_2$. We are currently repeating the calculation using r_1, r_2 , and r_{12} coordinates in the hope of obtaining better lower bounds as well as reliable upper bounds on the phase shift.

We have also seen from the values of $\eta_0(l, \text{MP})$ that the usual close-coupling approximation is hopeless in the e^+H problem because of the slow convergence in l and also in n . For problems for which a large number of target states contributes collectively the close-coupling approximation is not reliable and the analytical-variational type method used here will generally be much more convenient.

The present study further clarifies some aspects of the applicability of the minimum principle. Once the operator $Q[H+HG^PH]Q$ and the wave function $P\Psi^P$ are constructed, the variational problem involved in a MP calculation is completely identical to that of the Rayleigh-Ritz method for bound-state problems. Contrary to variational principles of the Kohn and Hulthén type, one obtains a rigorous lower bound on the phase shift which improves monotonically as the trial function is refined. Therefore one can trivially decide which of two trial functions is the better one, and, in particular, one has an unambiguous criterion for choosing between different sets of nonlinear variational parameters.

The construction of G^P is not difficult for the present problem, but it is expected to be more involved for multichannel problems with or without exchange effects. The integrals involving G^P also require a large portion of the computer machine time although they usually contribute only a small fraction to the final phase shift. Therefore, except for a very simple problem such as e^+H scattering, it is desirable to set up the calculation in such a way that, if possible, an explicit evaluation of G^P can be avoided.

¹⁹ B. H. Brandsen, Proc. Roy. Soc. (London) **A79**, 190 (1962).

In the present approach, one first calculates η_0^P and then uses the minimum-principle formulation to calculate the quantity Δ_θ which effectively takes us from η_0^P to η . The worst possible situation is that for which η_0^P is large and negative and $\eta_0 \approx 0$. In that case a small fractional error in Δ_θ introduces a large fractional error in the estimate of η_0 . This situation is precisely that with which we are faced in the present problem, and one would generally hope to do rather better than we have done here. In particular, for e^+H scattering with $L \geq 1$, the accuracy of η_L should be comparable with that of Δ_θ . If $\eta_0 - \eta_0^P \ll |\eta_0^P|$, the accuracy of η_0 should be much greater than the accuracy of Δ_θ ; this favorable situation occurs in e^-H scattering.

Considering the various difficulties discussed above, the values of the phase shift given in Table III compare reasonably well with the result of Schwartz²—we certainly had not expected to improve upon his results—and we may now proceed to study the higher partial waves¹⁵ where little is known, to e^-H scattering for various partial waves, and to other scattering systems of interest.

A very interesting article has recently been published by Sugar and Blankenbecler.²⁰ It can however readily be shown that their expression for the upper bound on $\cot(\eta - \theta)$ is *identical* to the bound expression given earlier¹² and used here. [See Eqs. (2.10) and (2.11).] The word identical is used in the sense that the same trial function gives the same result. (Some intermediate calculations could be performed differently.) A similar remark holds for their bound on elements of the K matrix.

Note added in proof. As noted above, there will be occasions, particularly for more complicated problems, when there will be some advantages associated with methods that do not demand the explicit evaluation of G^P . (This can be true even for variational bounds that are formally equivalent to that used in this paper.) One possibility is rather obvious. In the present (relatively simple) context, for example, the problem of the determination of G^P reduces to the problem of the determination of $\{g^P(r_2, r_2') r_2 r_2'\}$. Now in fact we do not need this latter quantity, but only integrals involving this quantity. Consider then the determination of

$$I(r_2) \equiv \int \{g^P(r_2, r_2') r_2 r_2'\} f(r_2') dr_2',$$

where $f(r_2')$ is some known function. With $L(r_2)$ the differential operator appearing in the differential equation [following (2.16)] that defines $\{g^P(r_2, r_2') r_2 r_2'\}$, it follows that

$$L(r_2)I(r_2) = -f(r_2).$$

$I(r_2)$ can therefore be obtained directly as the solution of an inhomogeneous differential equation without g^P

(or equivalently G^P) having been obtained. The situation will be more complicated when identical particles are involved in a process. A number of possible ways of avoiding the explicit use of G^P have been explored^{20, 20a}; this should remain a fruitful avenue of research.

ACKNOWLEDGMENTS

We would like to express our deep appreciation to Dr. P. G. Burke, Dr. K. Smith, Dr. P. A. Fraser, and Dr. R. P. McEachran for providing us with the various close coupling approximation results that we needed. The excellent assistance of I. Aronson with the coding of the program on the IBM-7094 is very much appreciated. Finally, we want to thank Dr. C. Kleinman for checking some of the matrix elements and for some helpful discussions.

APPENDIX A: SOME DETAILS OF THE CALCULATION

We summarize in this Appendix the procedure used in the choice of nonlinear parameters, the random function generator routine used as a partial test of the correctness of the minimum obtained, and the use of an alternate form of trial function to examine the long-range effect.

The nonlinear parameters b_{li} and d_{li} in the expression for $Q\Psi_l$ are chosen on the basis of a very primitive searching procedure in which each pair of b_{li} and d_{li} is varied systematically while the rest of the parameters are held fixed. Meaningful results can be expected even with such a rudimentary form of searching precisely because the minimum principle asserts that the larger the phase shift the better it is. As each additional term is introduced into the trial function, its nonlinear parameters are varied while the rest of the parameters are held fixed. The old parameters are then revaried, again *one pair at a time*, for further improvement. Two important simplifications are found possible in the course of the search. Firstly, the coupling between states of different l is not very sensitive to the values of the nonlinear parameters, and thus they are determined for each l separately; only the linear parameters are re-determined in the final calculation which includes coupling between all states with $l \leq 5$. The coupling significantly affects the values of the phase shift; the reason that the results are nevertheless relatively insensitive to the values of the nonlinear parameters may be that the off-diagonal elements of \mathbf{K} which couple different l states do not involve the kinetic energy (derivative) term but only the relatively smooth potentials to be integrated over. The second simplification is to neglect during the search that part of \mathbf{K} which involves the Green's function G^P , denoted by \mathbf{G} . \mathbf{G} has to be evaluated numerically and thus requires over 90% of the

²⁰ R. Sugar and R. Blankenbecler, Phys. Rev. **136**, B472 (1964). [Also, L. Rosenberg, Phys. Rev. **138**, B1343 (1965).]

^{20a} Y. Hahn, Phys. Rev. **139**, B212 (1965), Appendix A; and M. Gailitis (unpublished), and P. G. Burke (unpublished).

total machine time, although its contribution to Δ is only a few percent. The rest of the integrals in \mathbf{K} can be calculated analytically for the simple form of the trial function we have chosen.

The choice of the trial function $Q\Psi_t$ as given by (2.12) is a reasonable one since it is then possible to include two nonlinear parameters for each linear parameter. On the other hand, the nonlinear parameters are very difficult to search for, and there is ever present the danger that one may fall into one of the local minima that can be present in the multidimensional parameter space of the b_{ii} 's and d_{ii} 's. To check on the possibility that at a given stage in the calculation we have not fallen into a local minimum from which it is difficult to emerge by studying small variations of the nonlinear parameters, we used the random function generator routine which generates widely varying sets of values of the b_{ii} 's and d_{ii} 's. None of the sets however gave values of Δ lower than the one obtained by the search procedure, which indicates that the search procedure had led to the region which contained the absolute minimum.

We have also examined the effect on Δ of the variation in the form of the trial function. Since the importance of the long-range interaction of the form r^{-4} is well understood²¹ at low energy, we included in $Q\Psi_t$ the inverse-power behavior asymptotically for ω_{ii} . Such forms were essential in obtaining convergence at the zero energy variational calculation.² The results differ very little for two forms of trial function at $ka_0=0.2$.

APPENDIX B: ERROR ESTIMATION AND EXTRAPOLATION

We now discuss the method used in estimating the correction to $\eta_0(l, \text{MP})$ due to the poor trial function $Q\Psi_t$, and the extrapolation procedure used to obtain $\tilde{\eta}_0(l=\infty)$.

Due to the strong coupling between different l states, discussed in Appendix A, and due to the complexity of the error function $Q\Omega \equiv Q\Psi_t - Q\Psi$, it was found to be very difficult to make precise corrections. For the purpose of learning how to estimate the correction, we have constructed several sets of test cases such that successive sets are an improvement over the previous sets in that more terms are added to the previous sets. Our problem is then to see how well we can predict the (known) $\Delta(l)$ for the better sets using the values from the poorer sets.

Some readily available values to be used in the predictions are $\Delta_i^{(0)}$, $\Delta^{(0)}(l)$, and $\bar{\Delta}_i^{(0)}$. The superscript zero denotes the deletion of the \mathbf{G} term in \mathbf{K} , and the bar denotes the value obtained by using the trial function of the set to be predicted. (For the true problem, we still can obtain $\bar{\Delta}_i^{(0)}$ by including a large number of

linear parameters, and the value $\bar{\Delta}_i^{(0)}$ obtained can thus be regarded as "exact.") $\Delta^{(0)}(l, \text{MP})$ is obtained by including states up to l' , while $\Delta_{l'}^{(0)}(\text{MP})$ is for the l' state only.

For a diverse choice of test sets, a correction formula which gave reasonably accurate predictions was found to be

$$\tilde{\Delta}(l) = \Delta(l, \text{MP}) [1 + (\Delta^{(0)}(l, \text{MP}))^{-1} \sum_{l'=0}^l F_{l'} D_{l'} W_{l'}],$$

where

$$F_{l'} = [\Delta^{(0)}(l', \text{MP}) - \Delta^{(0)}(l' - 1, \text{MP})],$$

$$D_{l'} = [\bar{\Delta}_{l'}^{(0)} - \Delta_{l'}^{(0)}(\text{MP})] / \Delta_{l'}^{(0)}(\text{MP}),$$

$W_{l'} =$ slowly varying function of l' , $D_{l'}$, and $\Delta_{l'}^{(0)}(\text{MP})$.

Various choices are again possible for the functional form of $W_{l'}$, and we have found that $W_{l'} = [1 - (l'^2 \ln D_{l'}) / 4]^{1/2}$ seems to give a good fit with an approximate accuracy of 30% of the corrections in each test case.

Obviously the procedure described above is far from conclusive. However, the use of $\tilde{\eta}_0(l)$ obtained by including the correction is found essential in extrapolation to $l > 5$; the rigorous values $\eta_0(l, \text{MP})$ consistently underestimate the contribution from states with $l > 5$.

The convergence of η_0 in l is very slow for the e^+H problem. This difficulty is not new, and Schwartz,²² for example, obtained the l dependence of the forms l^{-4} and l^{-6} for the singlet and triplet states, respectively, of the two-electron bound-state system. His argument on the singularities near $r_1 \approx r_2$ may be taken over readily for the present case but with an important modification due to the strong coupling that exists between states of different l . By explicit numerical calculation, we have found that the function $F_{l'}$, which takes into account the coupling effect, behaves for large values of l' very roughly as

$$F_{l'} \sim l' \Delta_{l'}^{(0)}(\text{MP}).$$

Therefore it may be reasonable to expect that $\eta_0(l)$ will converge as l^{-3} . Although an l^{-4} dependence is not entirely ruled out, we made a two-parameter fit of $\tilde{\eta}_0(l)$ using the form

$$A \sum_{l'=l+1}^{\infty} (l' + B)^{-3}.$$

The value $B=1.30$ is adequate for the various energies considered, but we had to use $A=0.42, 0.93,$ and 1.24 for $ka_0=0.2, 0.4,$ and $0.6,$ respectively. Because of the large error contained in $\tilde{\eta}_0(4)$ and $\tilde{\eta}_0(5)$, the final phase shift $\tilde{\eta}_0$ cannot be determined very accurately.

We believe that, although our result is in fair agreement with that of Schwartz which is presumably the most reliable so far, more accurate lower as well as upper bounds should help further clarify the situation since there are some uncertainties yet to be investigated in the methods employed by various authors.

²¹ L. Spruch, T. F. O'Malley, and L. Rosenberg, Phys. Rev. Letters **5**, 375 (1960); T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).

²² C. Schwartz, Phys. Rev. **126**, 1015 (1962).

APPENDIX C: MATRIX ELEMENTS

The vectors \mathbf{N} and the matrix \mathbf{K} appearing²³ in (2.19) are defined as

$$N_p \equiv N_{il} = \int_0^\infty dr_2 \omega_{il}(x_2) U_{il}(r_2) u_0^P(r_2) (2ma_0/\hbar^2),$$

$$K_{pq} \equiv K_{il,jl'} = M_{il,jl'} - G_{il,jl'},$$

with $G_{il,jl'}$ defined by

$$G_{il,jl'} = \int_0^\infty r_2' r_2 dr_2 dr_2' \omega_{il}(x_2) U_{il}(r_2) g^P(r_2, r_2') U_{jl'}(r_2') \omega_{jl'}(x_2') (2ma_0/\hbar^2).$$

The quantities $M_{il,jl'}$ and U_{il} can be conveniently defined in terms of the following expressions:

$$Z(m, n, b; r) = \int_0^\infty dr' \begin{cases} r' < r \\ r' > r \end{cases} \frac{r'^n}{r} e^{-br'},$$

$$I(m; n, b; n, d) = \frac{1}{a_0} \int_0^\infty dr Z(m, n, b; r) r^n e^{-dr} = \frac{(n-m-1)!}{(b+d)^{2n}} \left\{ b^{-1} \sum_{s=0}^{n-m-1} \frac{(2n-1-s)!}{(n-m-1-s)!} g^s + d^{-1} \sum_{s=0}^{n-m-1} \frac{(2n-1-s)!}{(n-m-1-s)!} h^s \right\},$$

with $g = 1 + d/b$ and $h = 1 + b/d$. We give explicitly the expressions for U_{il} and $M_{il,jl'}$ for $l, l' = 0, 1$, and 2 . The matrix elements for $l, l' \geq 2$ will be supplied on request. It is simply a matter of performing some integrals involving Legendre polynomials. We set $(2m/\hbar^2) = 1$ and $a_0 = 1$ in the following.

$$l=0: \quad U_{i0}(r_2) = -4[Z(0, 2, A_{i0}; r_2) - a_i Z(0, 2, 2; r_2)],$$

$$M_{i0,j0} = \frac{4}{(D_{i0,j0})^3} \left[\frac{1}{(B_{i0,j0})^3} - \frac{8}{(A_{i0} A_{j0})^3} \right] [k^2 - D_{i0,j0} - d_{i0} d_{j0} - A_{i0} A_{j0}^3 / [(A_{i0} A_{j0})^2 + 4(B_{i0,j0})^2 + 2B_{i0,j0} A_{i0} A_{j0}]] \\ - 2I(0, 2, B_{i0,j0}; 2, D_{i0,j0}) + 2a_j I(0, 2, A_{i0}; 2, D_{i0,j0}) + 2a_i I(0, 2, A_{j0}; 2, D_{i0,j0}) - 2a_i a_j I(0, 2, 2; 2, D_{i0,j0}),$$

$$l=1: \quad U_{i1}(r_2) = (4/\sqrt{3})Z(1, 3, A_{i1}; r_2),$$

$$M_{i1,j1} = [(4!)^2 / (B_{i1,j1} D_{i1,j1})^5] [k^2 - 1 - b_{i1} b_{j1} - d_{i1} d_{j1} + \frac{1}{2}(B_{i1,j1} - D_{i1,j1})] \\ - 2I(0, 4, B_{i1,j1}; 4, D_{i1,j1}) - \frac{4}{3}I(2, 4, B_{i1,j1}; 4, D_{i1,j1}), \\ M_{i0,j1} = (2/\sqrt{3})I(1, 3, B_{i0,j1}; 3, D_{i0,j1}) - (2/\sqrt{3})a_i I(1, 3, A_{j1}; 3, D_{i0,j1}).$$

$$l=2: \quad U_{i2}(r_2) = -(4/\sqrt{5})Z(2, 4, A_{i2}; r_2),$$

$$M_{i2,j2} = [(6!)^2 / (B_{i2,j2} D_{i2,j2})^7] [k^2 - 1 - b_{i2} b_{j2} - d_{i2} d_{j2} + \frac{1}{3}(B_{i2,j2} - D_{i2,j2})] \\ - 2I(0, 6, B_{i2,j2}; 6, D_{i2,j2}) - (4/7)I(2, 6, B_{i2,j2}; 6, D_{i2,j2}) - (4/7)I(4, 6, B_{i2,j2}; 6, D_{i2,j2}),$$

$$M_{i1,j2} = (4/\sqrt{15})I(1, 5, B_{i1,j2}; 5, D_{i1,j2}) + (6/7)(\frac{2}{3})^{1/2}I(3, 5, B_{i1,j2}; 5, D_{i1,j2}),$$

$$M_{i0,j2} = -(2/\sqrt{5})I(2, 4, B_{i0,j2}; 4, D_{i0,j2}) + (2/\sqrt{5})a_i I(2, 4, A_{j2}; 4, D_{i0,j2}).$$

We have used the following notation:

$$A_{il} = 1 + b_{il}, \quad a_i = 8A_{i0}^{-3},$$

$$B_{il,jl'} = b_{il} + b_{jl'}, \quad D_{il,jl'} = d_{il} + d_{jl'}.$$

²³ Throughout this Appendix, we have (inadvertently) interchanged the order of the indices i and l as compared to the notation of the remainder of the paper.