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Higher Partial Waves in Positron-Hydrogen Scattering*†‡

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The minimum-principle (MP) formulation of scattering theory is applied to the study of the scattering of positrons by atomic hydrogen for a number of incident energies between 0 and 6.8 eV, the threshold for pickup. Rigorous lower bounds, η_1 (MP) and η_2 (MP), are obtained on the p-wave ($L=1$) and d-wave ($L=2$) phase shifts, η_1 and η_2. The method requires the exact numerical solution of the scattering wave function and of the Green's function of the static (one-body) equation, and the orthogonalization of the trial function $Q\Psi_t$ to the ground-state wave function; at that stage the method proceeds as in a standard variational calculation. $Q\Psi_t$ includes contributions from hydrogenic states with angular momenta $l_1=0,1,2$, and 3 for $L=1$, and $l_1=0,1$, and 2 for $L=2$; the associated radial functions contain arbitrary variational parameters, as do the radial functions associated with the positron. Contributions from each l_1 to the total η_L (MP), and the effects of the coupling of different l_1, are studied, and extrapolation estimates of η_1 and η_2 are obtained. The rigorous (variational) bounds and the estimates based on extrapolation are compared with close-coupling and other previous estimates and, at very low energies, with predictions based on long-range polarization effects.

1. INTRODUCTION

It is relatively simple to apply the zero-energy form of the minimum principle (MP) or variational bound formalism of scattering theory[1] to the determination of the ($L=0$) scattering length A for the (zero-energy) scattering of positrons by atomic hydrogen.[2,3] The determination of A for e^+H gives us not only the $L=0$ scattering at the incident energy $E'=0$ but also the scattering for very small E', for the next two terms in the expansion $ka_0 \cot\eta$ are known *exactly*[4] if one knows A and the electric-dipole polarizability α_1 of the H atom. Furthermore, the *leading* terms in the expansion of $\tan\eta$ for $L\geq 1$ follow from a knowledge of α_1.[5,6] For $L\geq 1$, we will not therefore be concerned with $E'=0$ since the quantity that plays the role of the scattering length is known exactly.

For $E'>0$, the form of the MP is somewhat more complicated,[7] but it has been applied[8,9] to e^+H $L=0$ scattering for $0\leq E'\leq 6.8$ eV, where the upper limit is the threshold for pickup. The present paper is an application of the MP to the $L=1$ and $L=2$ scattering of positrons by atomic hydrogen.

2. PROCEDURE FOR CALCULATING WITH THE IMPROVED MINIMUM PRINCIPLE

In this section we use the improved minimum principle[7] for single-channel scattering to formulate a method for obtaining a variational lower bound on the phase shift η_L for an arbitrary total angular momentum L. Although the formulation is given for e^+H scattering it is also applicable, with modifications which are re-

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[1] L. Spruch and L. Rosenberg, Phys. Rev. **116**, 1034 (1959).

[2] L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960).

[3] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[4] L. Spruch, T. F. O'Malley, and L. Rosenberg, Phys. Rev. Letters **5**, 375 (1960).

[5] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).

[6] T. F. O'Malley, L. Rosenberg, and L. Spruch, Phys. Rev. **125**, 1300 (1962).

[7] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **130**, 381 (1963). This formulation will be referred to as the improved minimum principle to distinguish it from an earlier crude version given by L. Rosenberg and L. Spruch, Phys. Rev. **121**, 1720 (1961).

[8] Y. Hahn and L. Spruch, Phys. Rev. **140**, A18 (1965).

[9] Preliminary results for $L=0$ e^+H scattering 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, July 1963*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 312.

quired to account for the effects of the Pauli principle, to e^-H scattering.

We are interested in energies too low for positronium formation and therefore *a fortiori* too low for excitation of the hydrogen atom. Virtual positronium formation[2] and virtual excitation[10] can nevertheless play significant roles in the description of the H atom during the course of the scattering. It is however somewhat difficult to take both effects into account and some decision has to be made as to which effect will be concentrated on. The decision is not simply a matter of which effect is more important but depends upon the ease with which the calculation can be performed. We will now examine this point.

The coordinates of the electron and positron are denoted by $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, where

$$\mathbf{r}_i=(r_i,\theta_i,\varphi_i)=(r_i,\hat{r}_i)=(r_i,\Omega_i)\,,\quad i=1,2\,, \tag{2.1a}$$

or almost equivalently,

$$r_1,\ r_2,\ \theta_{12},\ \text{and 3 Eulerian angles}, \tag{2.1b}$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. Another possible set of coordinates is

$$r_1,\ r_2,\ r_{12},\ \text{and 3 Eulerian angles}. \tag{2.2}$$

The latter set of coordinates has the advantage that it takes into account correlation in position which involves contributions from states with high l_1 values, but we preferred the set given by (2.1) for three reasons.

(1) We require a trial function $Q\Psi_t$ which is orthogonal to the hydrogen ground state, and it is simpler to choose such trial functions if one uses the set given by (2.1).

(2) For a total angular momentum $L=0$, the trial function will be independent of the Eulerian angles, and the set given by (2.1b) reduces to r_1, r_2, and θ_{12}, while the set given by (2.2) reduces to r_1, r_2 and r_{12}. The Hamiltonian H is somewhat more complicated for the latter set and the orthogonalization condition is more difficult to satisfy, but the calculation is manageable. However, for $L>0$ the Hamiltonian and orthogonalization become very much more complicated for the coordinate set given by (2.2) and the calculation may be too cumbersome to handle.[11] (It should be noted that a calculation using a Kohn variational scheme similar to the one described in Ref. 3 is being applied[12] to the e^+H and e^-H scattering problem for $L=1$.)

(3) With the set (2.2) it is easier to include the ground and excited states of positronium, while with the set (2.1) it is possible to study the effect of inclusion of each excited state of the target in the trial function $Q\Psi_t$. The latter provides us with a useful check on our program for it enables us to compare our results with those obtained from a close-coupling approximation calculation.

The starting point of our formulation is the MP, with the subtraction terms deleted, for a total angular momentum L and a total angular momentum projection M, which is given by

$$\begin{aligned}(k\hbar^2/2m)[\cot(\eta_L-\theta)-\cot(\eta_L{}^P-\theta)]\\ \leq 2(P\Psi_L{}^P,PHQ\Psi_{Lt})+(Q\Psi_{Lt},Q[\mathfrak{H}-E]Q\Psi_{Lt})\,.\end{aligned} \tag{2.3}$$

We have dropped the index M on the wave functions since the scattering is independent of the orientation of the system in space. For notational convenience, the index L will also often be deleted. η and η^P are the exact and the static phase shifts, respectively, and the normalization constant θ satisfies $0\leq\theta<\pi$. k is defined by $\hbar^2k^2/2m=E'=E-E_{T0}$, where E_{T0} is the ground-state energy of the target. $P\Psi^P$ is the exact static approximation scattering wave function given by

$$P\Psi^P=R_{10}(r_1)u_L{}^P(r_2)\mathcal{Y}_{L0L}{}^M(\Omega_{12})/r_2\,, \tag{2.4}$$

where the projection operator P is given by

$$P=R_{10}(r_1)\mathcal{Y}_{L0L}\rangle\langle R_{10}(r_1)\mathcal{Y}_{L0L}, \tag{2.5}$$

and where R_{10} is the radial part of the ground-state wave function of the hydrogen atom given by

$$R_{10}(r_1)=2a_0{}^{-3/2}e^{-r_1/a_0}\,, \tag{2.6}$$

with a_0 the Bohr radius. $\mathcal{Y}_{L0L}$ is defined by

$$\begin{aligned}\mathcal{Y}_{Ll_1l_2}{}^M(\Omega_{12})=\sum_{m_1,m_2}C_{l_1l_2}(L,M;m_1,m_2)\\ \times Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)\,,\end{aligned} \tag{2.7}$$

where the $C_{l_1l_2}(L,M;m_1,m_2)$ are the Clebsch-Gordan coefficients. $u_L{}^P(r_2)$, which is regular at the origin and subject to the boundary condition

$$\begin{aligned}u_L{}^P(r_2)\underset{r_2\to\infty}{\longrightarrow}-kr_2[\sin\eta_L{}^Pn_L(kr_2)\\ -\cos\eta_L{}^Pj_L(kr_2)]/\sin(\eta_L{}^P-\theta)\,,\end{aligned} \tag{2.8}$$

(where j_L and n_L are spherical Bessel and spherical Neumann functions, respectively) is a solution to the one-particle equation

$$[-d^2/dr_2{}^2+L(L+1)/r_2{}^2+V_{00}(r_2)-k^2]u_L{}^P(r_2)=0\,, \tag{2.9}$$

where

$$V_{00}(r_2)=(2/a_0)(1/a_0+1/r_2)\exp(-2r_2/a_0)\,. \tag{2.10}$$

$(\hbar^2/2m)V_{00}(r_2)$ is the static potential. Thus, the determination of the static approximation phase shift η^P is a simple matter with the use of a computer. In terms of the projection operator $Q=1-P$, the operator $\mathfrak{H}$ appearing in (2.3) is defined by

$$\begin{aligned}\mathfrak{H}(E,\theta)\equiv\mathfrak{H}\equiv Q\left[H+HP\frac{1}{P(E-H)P}PH\right]Q\\ \equiv Q[H+HG_L{}^PH]Q\,,\end{aligned} \tag{2.11}$$

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[10] S. Geltman, Phys. Rev. **119**, 1283 (1960); K. Smith, R. P. McEachran, and P. A. Fraser, *ibid.* **125**, 553 (1962).

[11] C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).

[12] R. L. Armstead and C. Schwartz (private communication).

where the Hamiltonian H is given by

$$H=-(\hbar^2/2m)(\nabla_{\mathbf{r}_1}{}^2+\nabla_{\mathbf{r}_2}{}^2) \\ -e^2(1/r_1-1/r_2+1/r_{12}), \quad (2.12)$$

and where the static Green's function $G_L{}^P$ is constructed from the regular and irregular solution of Eq. (2.9) and is given by

$$G^P(r_1,r_2,\Omega_{12};r_1',r_2',\Omega_{12}')=R_{10}(r_1)\mathcal{Y}_{L0L}(\Omega_{12})R_{10}(r_1') \\ \times(\mathcal{Y}_{L0L}(\Omega_{12}')g(r_2,r_2'), \quad (2.13)$$

where

$$g(r_2,r_2')=-\frac{2m}{k\hbar^2}[u_{\mathrm{reg}}{}^P(r_{2<})u_{\mathrm{irreg}}{}^P(r_{2>})-\cot(\eta^P-\theta) \\ \times u_{\mathrm{reg}}{}^P(r_2)u_{\mathrm{reg}}{}^P(r_2')]\frac{1}{r_2r_2'}. \quad (2.14)$$

The second term in (2.14) is included to make it asymptotically proportional to $\sin(kr_2-\frac{1}{2}L\pi+\theta)$ as is required, and $u_{\mathrm{reg}}{}^P$ and $u_{\mathrm{irreg}}{}^P$ are subject to the boundary conditions that as $r_2\to\infty$

$$u_{\mathrm{reg}}{}^P(r_2)\to-kr_2[n_L(kr_2) \\ -\cot(\eta_L{}^P)j_L(kr_2)]\sin\eta_L{}^P, \quad (2.15a)$$

$$u_{\mathrm{irreg}}{}^P(r_2)\to-kr_2[j_L(kr_2) \\ -\cot(\eta_L{}^P)n_L(kr_2)]\sin\eta_L{}^P. \quad (2.15b)$$

Before giving the form of the trial function we note that for $L>0$ and for $l_1>0$, where l_1 is the orbital angular momentum of the atomic electron, more than one value of l_2 is allowed by the usual vector additions, subject to parity and other selection rules, to combine with l_1 to give L. In Table I we designate a pair of values of l_1, l_2 by γ. We take a trial function of the following form

$$Q\Psi_t(r_1,\Omega_1;r_2,\Omega_2) \\ =\sum_{i,\gamma}c_{i\gamma}\omega_{i\gamma}(r_{1/a_0})\chi_{i\gamma}(r_{2/a_0}) \\ \times\mathcal{Y}_{Ll_1,l_2}(\Omega_{12})/(r_1r_2a_0{}^{1/2})=\sum_p c_pQ\Psi_{tp}, \quad (2.16)$$

where the summation over i indicates that for any fixed L, i can vary from one up to some arbitrary value which can depend on γ, and where in the latter sum we let the index p stand for both indices i and γ. The c_p are the linear variational parameters, while

$$\omega_p(x_1)=x_1{}^{l_1+1}\exp(-b_px_1) \\ -[8(1+b_{i0})^{-3}]x_1\exp(-x_1)\delta_{0l_1} \quad (2.17a)$$

and

$$\chi_p(x_2)=x_2{}^{l_2+1}\exp(-d_px_2), \quad (2.17b)$$

where $x_i=r_i/a_0$ and where δ_{0l_1} is the Kronecker delta. The distinction between $l_1=0$ and $l_1\neq0$ is a consequence of the fact that for $l_1\neq0$ the requirement that the trial function $Q\Psi_t$ be orthogonal to R_{10} is automatically accomplished by the presence of the $\mathcal{Y}_{Ll_1l_2}$, while for $l_1=0$ one must choose the radial function $\omega_p(r_1)$ to be orthogonal to R_{10}. The b_p and d_p are nonlinear parameters.

TABLE I. Values for the labeling index γ for the possible sets of values of l_1 and l_2 for the limited range of values of l_1 considered.

$L=1$		γ	$L=2$	
l_1	l_2		l_1	l_2
0	1	0	0	2
1	0	1	1	1
1	2	2	1	3
2	1	3	2	0
2	3	4	2	2
3	2	5	2	4
3	4	6		

The $1/r_{12}$ term is expanded in terms of Legendre polynominals as

$$1/r_{12}=\sum_{\lambda=0}^{\infty}(r_<{}^{\lambda}/r_>{}^{\lambda+1})P_\lambda(\hat{r}_1\cdot\hat{r}_2)=\sum S_\lambda P_\lambda, \quad (2.18)$$

where $r_<$ and $r_>$ are the smaller and larger, respectively, of r_1 and r_2, and since $1/r_{12}$ does not couple states of different L or M, one has the requirements,

$$(1)\qquad(-1)^{l_1+l_2}=(-1)^{l_1'+l_2'}, \quad (2.19)$$

$$(2)\quad(-1)^{l_i+l_i'+\lambda}=1,\quad i=1\text{ or }2 \quad (2.20)$$

and

$$(3)\quad l_i+\lambda\geq l_i'\geq|l_i-\lambda|,\quad i=1\text{ or }2, \quad (2.21)$$

where l_1, l_2, and l_1', l_2' refer to the initial state and to the final state, respectively. The total angular momentum L is restricted by

$$l_1+l_2\geq L\geq|l_1-l_2|. \quad (2.22)$$

The integrals occurring in the MP involve the f_λ defined by

$$f_\lambda\equiv f_\lambda(l_1,l_2,l_1',l_2';L)\equiv(\mathcal{Y}_{Ll_1l_2}{}^M,P_\lambda\mathcal{Y}_{Ll_1'l_2'}{}^M); \quad (2.23)$$

the f_λ are tabulated by Percival and Seaton[13] for all transitions for which $l_1\leq2$, $l_1'\leq2$. Explicitly, we have[13]

$$f_\lambda(l_1,l_2,l_1',l_2';L) \\ =(-1)^{l_1+l_2}(2\lambda+1)^{-1}C_{l_1l_1'}(\lambda,0;0,0)C_{l_2l_2'}(\lambda,0;0,0) \\ \times[(2l_1+1)(2l_2+1)(2l_1'+1)(2l_2'+1)]^{1/2} \\ \times W(l_1,l_2,l_1',l_2';L,\lambda). \quad (2.24)$$

An extensive tabulation of the C's and of the Racah coefficients, the W's, is given by Rotenberg *et al.*[14] The $\mathcal{Y}_{Ll_1l_2}$ are orthonormal, and as a consequence we have

$$f_0(l_1,l_2,l_1',l_2';L)=\delta_{l_1l_1'}\delta_{l_2l_2'}. \quad (2.25)$$

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[13] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. 53, 655 (1957).

[14] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3−j and 6−j Symbols* (The Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959).

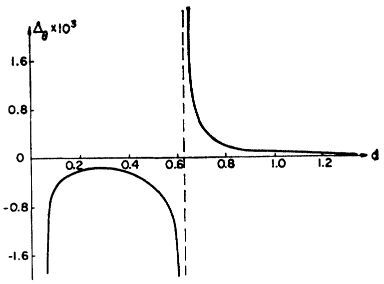

FIG. 1. An illustration of the spurious jump in Δ_θ when θ is chosen to lie between η^P and η. For an explanation of this illustration see the discussion following Eq. (2.32).

The f_λ also satisfy the symmetry relation

$$f_\lambda(l_1,l_2,l_1',l_2';L)=f_\lambda(l_1',l_2',l_1,l_2;L) \tag{2.26}$$

and the relationship

$$f_\lambda(l_1,l_2,0,L;L)=0 \quad \text{if} \quad l_1\neq\lambda. \tag{2.27}$$

Using $PHQ=P(-e^2/r_{12})Q$ and introducing

$$N_p\equiv(Q\Psi_{tp},Q[-e^2/r_{12}]P\Psi^P)(2ma_0/\hbar^2) \tag{2.28}$$

and

$$K_{pq}\equiv(Q\Psi_{tp},Q[H-E+(e^2/r_{12})G^P(e^2/r_{12})]Q\Psi_{tq}) \times(2ma_0/\hbar^2), \tag{2.29}$$

Equation (2.3) can be written as

$$ka_0[\cot(\eta-\theta)-\cot(\eta^P-\theta)]\le 2\mathbf{c}\cdot\mathbf{N}+\mathbf{c}\cdot\mathbf{K}\mathbf{c}, \tag{2.30}$$

where $\mathbf{c}$ and $\mathbf{N}$ are vectors and $\mathbf{K}$ is a real symmetric matrix whose order is equal to the number of trial functions, with the possible values of the index p, which comprises the indices γ and i, having been given some definite ordering. The elements of $\mathbf{c}$, the linear variational parameters, are determined for a given choice of the nonlinear parameters by minimizing the r.h.s. of Eq. (2.30). One immediately finds

$$\mathbf{c}=-\mathbf{N}\cdot\mathbf{K}^{-1} \tag{2.31}$$

so that

$$ka_0[\cot(\eta_L-\theta)-\cot(\eta_L{}^P-\theta)]\le-\mathbf{N}\cdot\mathbf{K}^{-1}\mathbf{N}\equiv\Delta_\theta. \tag{2.32}$$

Note that Δ_θ is independent of the normalization of the trial function, since $Q\Psi_{tp}$ enters quadratically in the numerator and in the denominator of Δ_θ.

Before giving the form of the integrals we discuss briefly the normalization constant θ. If θ is chosen to be such that

$$\eta^P<\theta<\eta, \tag{2.33}$$

then one has in principle one subtraction term on the right-hand side of Eq. (2.32), since the bound on η, which equals η^P when $Q\Psi_t=0$, will increase as more terms are included in the trial function $Q\Psi_t$, thus causing a sudden jump of $\cot(\eta-\theta)$ when $\eta=\theta$. This spurious subtraction should not be confused with one due to the presence of a bound state. In practice a sufficiently accurate wave function could easily take into account this subtraction[15] (or any finite number of subtractions). To avoid this, one can conveniently choose any θ outside the range given above. If, for example, θ is chosen as

$$\theta=\tfrac{1}{2}\pi+\eta^P, \tag{2.34}$$

the inequality given by Eq. (2.32) reduces to the simple form

$$ka_0\tan(\eta-\eta^P)\ge-\Delta>0, \tag{2.35}$$

where $\Delta=\Delta_{\theta=\frac{1}{2}\pi+\eta^P}$. The above choice of θ was motivated by the estimate that η is smaller than $\frac{1}{2}\pi+\eta^P$.

The illustration of the spurious jump when θ is chosen to lie between η^P and η is shown in Fig. 1. For $ka_0=0.3$ and $L=1$, $\eta_1{}^P=-0.00555$. To simplify the calculation we set $b_{i\gamma}=b_{11}=0.5$ and allow $d_{i\gamma}=d_{11}$ to assume values from 0.05 through 6.0. With $b_{11}=0.5$ and $d_{11}=0.2$ the best value of the phase shift is obtained as $\eta_1(\mathrm{MP})=0.00168$, and if θ is chosen as $\theta=-0.004$ the jump in Δ occurs when

$$0.62<d_{11}<0.64. \tag{2.36}$$

However, when θ is chosen outside the bound (2.33), say $\theta=\frac{1}{2}\pi+\eta_1{}^P$, and the above calculation is repeated, no such jump occurs; see Fig. 2. It should be mentioned that it is essential to have only *one* term in the trial function in order to see the jump.

This jump is not indicative of a real bound state; it is rather a spurious bound state of $\mathcal{H}(E,\theta)$ introduced by the particular choice of $\theta=-0.004$ for this particular problem. It should be emphasized that whether one uses this latter value of θ or uses $\theta=\frac{1}{2}\pi+\eta_1{}^P$, the value of $\eta_1(\mathrm{MP})$ in both cases converges to the true value of η_1 as the trial function is improved. Thus, one may choose any convenient θ in a particular problem for $ka_0>0$.

While in our problem we artifically introduced *one* "bound state" of $\mathcal{H}(E,\theta)$, in a variational calculation[16] one has an infinite number of eigenstates of H. It has

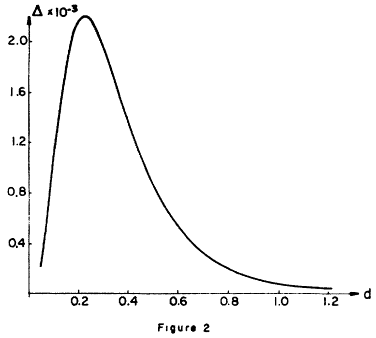

FIG. 2. A study of Δ when θ is chosen *outside* the range η^P to η. There is now no jump.

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[15] T. Ohmura, Phys. Rev. **124**, 130 (1961); L. Spruch, in *Lectures in Theoretical Physics*, Boulder, 1961, edited by W. E. Brittin, W. B. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1962), Vol. 4, p. 185.

[16] C. Schwartz, Ann. Phys. (N. Y.) **16**, 36 (1961).

TABLE II. The phase shifts in various approximations for $L=1$ and $L=2$. The B.S. and F.Mc results represent numerical solutions of the coupled equations by Burke and Smith,[a] and by Fraser and McEachran,[b] respectively; slightly different numerical procedures were used. The minimum principle (MP) results are in all cases either equal to or below the exact results and are generally rather close to them. The results labeled with an "all" preceding the state were obtained by using trial functions of the form given by Eqs. (2.17a) and (2.17b) in Eq. (2.16), and should be compared with the values immediately above them which were obtained by using exact hydrogenic wave functions in Eq. (2.16). The differences between these results are by no means negligible and show the inadequacy of the close-coupling approximation in the present problem. The dash on top of the numbers indicates the numbers in which there exists an uncertainty, and the numbers in parentheses give the uncertainty in the last digits.

L	States	Method	$ka_0=0.1$	$ka_0=0.2$	$ka_0=0.3$	$ka_0=0.4$	$ka_0=0.5$	$ka_0=0.6$	$ka_0=0.7$
1	$1s$		−0.00023	−0.00176	−0.00555	−0.01200	−0.02102	−0.03215	−0.04478
1	$1s+2p$	B.S.[a]	0.00465	0.01328	0.01995	0.02161	0.01768	0.00904	−0.00283
		F.Mc[b]	0.00462[c]	0.01325	0.01993	0.02159	0.01765	0.00900	−0.00289
		MP	0.00458	0.01316	0.01984	0.02146	0.01761	0.00868	−0.00314
1	$1s$+all p	MP			0.04103		0.06281		
1	$1s+3d$	F.Mc	$-0.0001\bar{9}\bar{8}$	$-0.0016\bar{1}$	$-0.0052\bar{6}$	$-0.0116\bar{1}$	$-0.0206\bar{0}$		$-0.0444\bar{1}$
		MP	−0.000198	−0.00161	−0.00526	−0.01161	−0.02060		−0.04441
1	$1s$+all d	MP			−0.00134		−0.01122		
1	$1s+4f$	MP			−0.00555		−0.02102		
1	$1s$+all f	MP			−0.00464		−0.01869		
1	$1s+2p+3d$	F.Mc	$0.0047\bar{2}$		$0.0209\bar{3}$	$0.0229\bar{4}$	$0.0191\bar{2}$		
		MP	0.00468(5)		0.02082(5)	0.02280(5)	0.01882(5)		
1	$1s$+all p+all d				0.05099		0.08809		
1	$1s+2p+3d+4f$	MP			0.02120		0.0200		
1	$1s$+all p+all d+all f	MP			0.05446		0.09796		
2	$1s$		−0.00000	−0.00002	−0.00014	−0.00051	−0.00134	−0.00282	−0.00507
2	$1s+2p$	F.Mc	0.00084[c]	0.00331	0.00698	0.01114	0.01504	0.01806	0.01991
		MP	0.00082	0.00324	0.00693	0.01106	0.01498	0.01782	0.01963
2	$1s$+all p	MP			0.01081		0.02589		
2	$1s+3d$	F.Mc	$1.2\bar{6}\times10^{-6}$		$-6.7\bar{5}\times10^{-5}$	$-0.0003\bar{7}\bar{1}$	$-0.0011\bar{3}$		
		MP	1.25×10^{-6}		-6.75×10^{-5}	−0.000371	−0.00113		
2	$1s$+all d				0.00040		0.00109		
2	$1s+2p+3d$	F.Mc	$0.0008\bar{6}\bar{7}$		$0.0072\bar{0}$	$0.0116\bar{0}$	$0.0157\bar{7}$		
		MP	0.000844(10)		0.00716(2)	0.01150(2)	0.01545(2)		
2	$1s$+all p+all d	MP			0.01180		0.03124		

[a] See Ref. 17. [b] See Ref. 18. [c] This result is an estimate obtained from the $1s+2p+3d$ result of F.Mc.

been shown by Schwartz[16] in the course of a variational calculation of elastic e^-H scattering for $ka_0>0$ and $L=0$ that as one increases the number of terms in the trial function, the "stationary" value of the phase shift does not converge smoothly, but may on occasion turn out to be grossly inaccurate, though normally, by proper interpretation of the calculations no difficulties will arise. However, with the MP it is possible to avoid this phenomenon altogether by eliminating the part of the continuous spectrum below E, and have the phase shift monotonically approach the true value.

Using Eqs. (2.4), (2.16), (2.18), and (2.27), N_p as defined by Eq. (2.28) can be written as

$$N_p=(-1/a_0^{1/2})\sum_{l_2} f_{l_1}(l_1,l_2,0,L;L)\int dr_2\,\chi_p(x_2)u^P(r_2)\times\int dr_1\,r_1\omega_p(x_1)S_{l_1}R_{10}(r_1)\,,\tag{2.37}$$

where as before $x_i=r_i/a_0$. K_{pq} as defined by Eq. (2.29) can be written as

$$K_{pq}=K_{a,pq}+K_{b,pq}+K_{c,pq}\,,\tag{2.38}$$

where

$$K_{a,pq}=(Q\Psi_{tp},[-(\hbar^2/2m)(\nabla_{r_1}^2+\nabla_{r_2}^2)-e^2(1/r_1-1/r_2)-E]Q\Psi_{tq})(2ma_0/\hbar^2)\,,\tag{2.39}$$

$$K_{b,pq}=(Q\Psi_{tp},[-e^2/r_{12}]Q\Psi_{tq})(2ma_0/\hbar^2)\,,\tag{2.40}$$

and

$$K_{c,pq}=(Q\Psi_{tp},[(e^2/r_{12})G^P(e^2/r_{12})]Q\Psi_{tq})\times(2ma_0/\hbar^2)\,.\tag{2.41}$$

Using (2.25), $K_{a,pq}$ can be written as

$$K_{a,pq}=\frac{2m}{\hbar^2}\int dr_1\,\omega_p(x_1)\omega_q(x_1)\int dr_2\,\chi_p(x_2)\times[t(l_2,r_2)+e^2/r_2-E]\chi_q(x_2)+\frac{2m}{\hbar^2}\int dr_2\,\chi_p(x_2)\chi_q(x_2)\int dr_1\,\omega_p(x_1)\times[t(l_1,r_1)-e^2/r_1]\omega_q(x_1)\,,\tag{2.42}$$

where

$$t(l_i,r_i)=(-\hbar^2/2m)[d^2/dr_i^2-l_i(l_i+1)/r_i^2]\,,\quad i=1\text{ or }2\,.\tag{2.43}$$

$K_{b,pq}$ may also be written as

$$K_{b,pq}=(-1/a_0)\sum_\lambda f_\lambda(l_1,l_2,l_1',l_2';L)\int dr_2\chi_p(x_2)\chi_q(x_2)\times\int dr_1\omega_p(x_1)S_\lambda\omega_q(x_1)\,.\tag{2.44}$$

Using Eqs. (2.13) and (2.27), $K_{c,pq}$ may be written as

$$K_{c,pq}=(e^2/a_0)\sum_{l_2,l_2'} f_{l_1}(l_1,l_2,0,L;L)f_{l_1'}(l_1',l_2',0,L;L)$$
$$\times\int dr_2 r_2 \chi_p(x_2)\int dr_1 \omega_p(x_1)S_{l_1}r_1R_{10}(r_1)$$
$$\times\int dr_2' r_2' \chi_q(x_2')\int dr_1' r_1' R_{10}(r_1')$$
$$\times S_{l_1'}\omega_q(x_1')g(r_2,r_2')\,, \quad (2.45)$$

where $g(r_2,r_2')$ is defined by (2.14).

3. RESULTS OF THE CALCULATION

A. Close-Coupling Approximation

If the total wave function is expanded in eigenstates of the hydrogen atom and if only a few low-lying states are retained, the exact phase shifts are available from various close-coupling approximation (C.C.A.) calculations.[17,18] In order to check our program and also to obtain an indication of how easily the MP can reproduce the known results, we obtained bounds on the phase shifts for a few cases for which we have a single excited state of the hydrogen atom with principal quantum number n and orbital angular momentum $l_1=n-1$. In particular, we obtained bounds on the $1s+2p$, $1s+3d$, and $1s+4f$ phase shifts for $L=1$ and on the $1s+2p$ and $1s+3d$ phase shifts for $L=2$. These states can be handled by our trial function (2.16) by simply setting $b_p=n^{-1}$, for each γ that corresponds to a definite l_1, in the trial function (2.16).

The form (2.16) cannot as it stands handle eigenstates with $n\neq l_1+1$, since these contain polynominals in x_1 with more than one term.

As shown in Table II the agreement between the $1s+2p$ phase shift obtained with the MP and the C.C.A. results of Burke and Smith, and of Fraser and McEachran is satisfactory in spite of the fact that no attempt was made to search for a better set of nonlinear parameters. The perfect agreement between the MP $1s+3d$ phase shifts and the phase shifts available from the C.C.A. for $L=1$ and $L=2$ provides a further check on the code. The agreement for $1s+2p+3d$ is also good. An important point to note here is that the phase shifts obtained with the MP are consistently either the same as or lower than and rather close to the values derived from the C.C.A., as expected. For the $1s+4f$ and $1s+2p+3d+4f$ phase shifts we do not have close-coupling results to make a comparison. The results in Table II labeled with an "all" preceding the state (e.g., $1s+$all p, $1s+$all d, etc.) were obtained by using trial functions of the form given by Eqs. (2.17a) and (2.17b) in Eq. (2.16), and should be compared with the values immediately above them (e.g., $1s+2p$, $1s+3d$, etc.) which were obtained by using exact hydrogenic wave functions in Eq. (2.16). The differences between these results are by no means negligible and show the inadequacy of the C.C.A. in the present problem.

It is worth noting that while for $ka_0>0.1$ the convergence of η(MP) occurred when the integration of N_p and $K_{c,pq}$ was carried out to $30a_0$, ($K_{a,pq}$ and $K_{b,pq}$ are integrated analytically out to infinity) it was necessary to integrate out to $60a_0$ and $80a_0$ for $L=1$ and for $L=2$, respectively, for $ka_0=0.1$. In the C.C.A. calculations,[18] it was found necessary to retain the contribution to the phase shift up to $r=60a_0$ for $L=1$ and $L=2$, for $ka_0=0.1$, while for $ka_0>0.1$ it was sufficient to retain contributions only up to $r=40a_0$. However, this phenomenon did not occur for $L=0$ either in the MP calculations[8] or in the C.C.A. calculations.[18] This points out that the major contribution to the phase shift for $ka_0=0.1$ comes from the long range contribution. This can be calculated *after* we have gone over to an equivalent one-body problem with a long-range $1/r^4$ potential in the Born approximation. In this approximation we have

$$k\tan\eta_L(\text{Born})=-\int_0^\infty [krj_L(kr)]^2(-\alpha_1/r^4)dr\,. \quad (3.1)$$

Now $j_L(kr)$ does not reach its maximum until $r\approx L/k$, i.e., $r=10La_0$ for $ka_0=0.1$, and even in the presence of the $1/r^4$ factor there will be significant contributions from large r. As L increases, not only does the contribution from large r play a significant role, but the contribution from small r decreases due to the r^{L+1} dependence of $krj_L(kr)$. It was found[18] that the contribution from $r=40a_0$ to $r=60a_0$ is 0.6 and 10.2% of the total phase shift for $L=1$ and $L=2$, respectively, for $ka_0=0.1$. From a physical point of view the necessity of having to integrate out further for $L>1$ and $ka_0=0.1$ is due to the effect of the centrifugal barrier. The repulsive nature of this barrier increases with L, and for small ka_0 the probability of the incident particle coming close to the scattering center is small so that one has to go out far in the integration to obtain the phase shift.

B. Threshold Energy Dependence of Phase Shifts

For scattering of charged particles by neutral polarizable systems, the usual form of effective range theory is not correct.[4-6] For $L\geq 1$ even the usual k^{2L+1} threshold energy dependence of Wigner is not correct. One has instead

$$\tan\eta_L=\pi[(2L+3)(2L+1)(2L-1)a_0]^{-1}\alpha_1k^2+\cdots\,, \qquad L\geq 1\,, \quad (3.2)$$

where the correction is of order k^3 for $L=1$ and of higher order for $L>1$. Since the electric polarizability α_1 of the hydrogen atom is given by $\alpha_1=4.5a_0^3$, we have

$$\tan\eta_L=J(L)(ka_0)^2\,, \quad (3.3)$$

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[17] P. G. Burke and K. Smith (private communication).

[18] P. A. Fraser and R. P. McEachran (private communication).

TABLE III. Comparison between $1s$+all p phase shifts obtained with the MP, and those obtained from Eqs. (3.3) and (3.4), the Born approximation for the long-range polarization potential which becomes exact as $ka_0 \rightarrow 0$.

Method / ka_0	MP $L=1$	long $L=1$	MP $L=2$	long $L=2$
0.05	0.0020	0.0024	0.00031	0.000338
0.10	0.0075	0.0094	0.0012	0.00135

where

$$J(1)=0.942,\quad J(2)=0.135,\quad J(3)=0.045,\quad \text{and } J(4)=0.020. \tag{3.4}$$

The values for the phase shifts for $ka_0=0.05$ and 0.1 obtained with (3.3) and (3.4) are compared in Table III with the values obtained with the MP. As expected, the agreement between the MP and the expressions (3.3) and (3.4) become better as one goes to lower ka_0 and to higher L. It is seen from Table III that the values for the phase shifts obtained with the MP are lower than the values obtained with the expressions (3.3) and (3.4), which is probably due to the choice of the particular form of the trial function given by (2.16) which does not easily take into account long-range effects since the individual terms do not have the correct asymptotic form.

C. The Ratio of Virtual Excitations

As seen from Table I, to each $\Delta^{(l_1)}$, [the superscript l_1 indicates the l_1 term contribution to Δ in (2.35) without coupling to other l_1 values] for $l_1>0$ and $L>0$, there corresponds more than one Δ_γ [the subscript γ indicates the γ term contribution to Δ in (2.35)]. The theoretical ratios obtained in Appendix A and the ratios obtained with the MP are given in Table IV. As seen from this table the difference between the values obtained from the MP and the theoretical predictions is a function of both the energy and the l_1 in question. Since the theory applies only to low scattering energies the dependence of the agreement between the theoretical ratios and the ratios obtained with the MP on the scattering energy is reasonable. Short-range forces become more important as l_1 becomes larger because the long-range forces associated with that l_1 then fall off faster and barrier effects for different l_1's may also contribute to the disagreement between the two ratios. In general, one expects that the agreement between the calculated and predicted ratios would improve as ka_0 decreases, as L becomes larger, and as l_1 becomes smaller. It may be worth noting that the ratios are expected to be more reliable than Eq. (3.2), since there will probably be some cancellation of errors and the ratios therefore serve as a much more stringent test on the code and on the powers of the MP.

TABLE IV. Comparison of the ratios of the contributions to $\Delta^{(l_1)}$ due to virtual excitation with L and l_1 fixed and l_2 taking on its different possible values, as obtained from the long-range approximation, Eqs. (A13) and (A14), and from the MP at very low energies. The agreement should improve as ka_0 decreases and as L increases.

			Ratios of contributions		
			Long range	MP	MP
L	l_1	l_2	$ka_0\approx0$	$ka_0=0.05$	$ka_0=0.1$
1	1	0, 2	1:2	1:1.93	1:1.86
2	1	1, 3	1:1.5	1:1.45	1:1.43
2	2	0, 2, 4	1:1.43:2.57	1:1.40:2.43	1:1.37:2.29

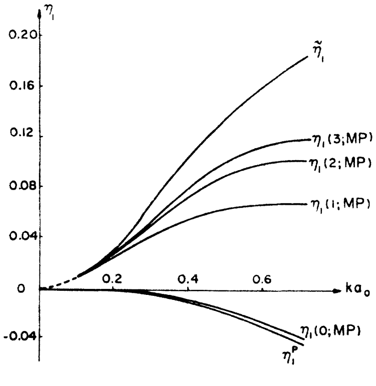

FIG. 3. The $L=1$ phase shift, in radians, in various approximations, versus ka_0. $\eta_1{}^P$ is the static approximation result. $\eta_1(l_1;\text{MP})$, the $L=1$ phase shift in the approximation in which the virtually excited hydrogenic states are restricted to angular momenta up to and including l_1, is a rigorous lower bound on η_1, the true $L=1$ phase shift. $\tilde{\eta}_1$ is our (still crude) estimate of η_1. It includes corrections to account for the inaccuracy of the trial function for the values of l_1(0, 1, 2, and 3) that were included and estimates of the contribution from $l_1>3$.

D. Rigorous Bound

For the limited form of the trial function (2.16) chosen, there occur two nonlinear parameters b_p and d_p

TABLE V. The rigorous lower bounds $\eta_L(l_1;\text{MP})$ on η_L in the approximation in which the virtually excited hydrogenic states are restricted to angular momenta up to and including l_1. The last column represents our best estimate $\tilde{\eta}$ obtained by extrapolation, of the exact phase shift η. The phase shifts are given in units of 10^{-2} rad. The number in parentheses gives the uncertainty in the last digit.

		Rigorous lower bounds				$\tilde{\eta}$
ka_0	L	$l_1=0$	$l_1=1$	$l_1=2$	$l_1=3$	
0.1	1	−0.021	0.743	0.805	0.823	0.86(1)
0.2	1	−0.163	2.370	2.764	2.892	3.2 (1)
0.3	1	−0.512	4.128	5.124	5.475	6.6 (4)
0.4	1	−1.100	5.555	7.341	8.008	11 (1)
0.5	1	−1.918	6.403	8.939	9.938	14 (1)
0.6	1	−2.917	6.700	9.876	11.162	17 (2)
0.7	1	−4.035	6.833	10.350	11.890	19 (2)
0.1	2	−0.000	0.121	0.123		0.13(0)
0.3	2	−0.013	1.081	1.181		1.4 (1)
0.5	2	−0.126	2.742	3.134		4.6 (5)
0.7	2	−0.471	4.240	5.700		10 (1)

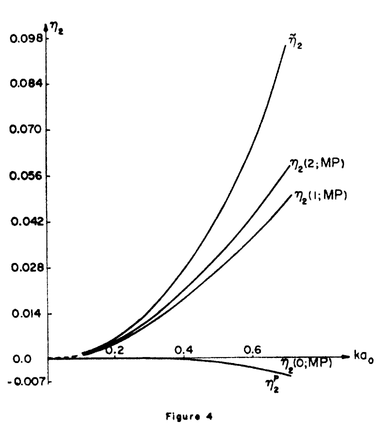

FIG. 4. The $L=2$ phase shift, in radians, in various approximations, versus ka_0. See caption for Fig. 3. (The values of l_1 considered in the trial function were 0, 1, and 2.) $\eta_2{}^P$ and $\eta_2(0;\text{MP})$ are indistinguishable on the graph.

for each linear parameter c_p. These nonlinear parameters were searched for by trying out different sets which were obtained by systematic variation of a particular b and d, and choosing that set which gives the largest value of the phase shift. As additional trial functions are introduced the old parameters are kept fixed while the new parameters are varied, and then the new parameters are kept fixed while the old parameters are researched.

Using these b's and d's and the c's as determined from Eq. (2.31) we obtained the values for $\eta_1(l_1;\text{MP})$ and $\eta_2(l_1;\text{MP})$ given in Table V and in Figs. 3 and 4. These phase shifts, the main results of the present paper, are ***rigorous lower bounds*** on the phase shifts for the artificial problems in which the hydrogen atom can only be virtually excited to states with a maximum value of l_1 and also on the true phase shift involving (virtual) excitation to all l_1 states.

E. Error Estimation for $l_1 \leq 2$, 3 and Extrapolation to Higher l_1's

Our choice of coordinates simplifies the problem of satisfying the orthogonality requirement, but it has the drawback that $\eta_L(l_1;\text{MP})$ as a function of l_1 does not converge very rapidly. Many l_1 states are required before one obtains a good representation of $Q\Psi_t$. However, before extrapolating to higher l_1's one must first obtain the magnitude of error in $\eta_L(l_1;\text{MP})$ for each l_1 due to the incorrectness of $Q\Psi_t$. It should be stressed that it is completely misleading to extrapolate to higher l_1's before correcting $Q\Psi_t$ for the l_1's included in $Q\Psi_t$. The crude estimate of η is designated by $\tilde{\eta}$ and is given in Table V and in Figs. 3 and 4. (For further details see Appendix B of Ref. 8.)

TABLE VI. The partial cross sections σ_0, σ_1, σ_2, and σ_3 in units of $\pi a_0{}^2$.

$ka_0 \diagdown \sigma_L$	$\sigma_0{}^{a}$	$\sigma_1{}^{b}$	$\sigma_2{}^{b}$	$\sigma_3{}^{c}$
0.1	9.000	0.077	0.002	0.001
0.2	3.497	0.307		0.002
0.3	1.239	0.581	0.044	0.005
0.4	0.360	0.843		0.009
0.5	0.062	0.901	0.169	0.014
0.6	0.001	0.941		0.021
0.7	0.002	0.847	0.368	0.028

[a] Obtained from Schwartz's phase shifts. (See Ref. 3.)
[b] Obtained from the phase shifts $\tilde{\eta}$ of Table V.
[c] The values for σ_3 were obtained from Eqs. (3.3) and (3.4).

F. Partial and Total Cross Sections

The partial and total cross sections are given in terms of the phase shifts by

$$\sigma_L = (4\pi/k^2)(2L+1)\sin^2\eta_L\,, \tag{3.5}$$

$$\sigma = \sum_{L=0}^{\infty} \sigma_L\,. \tag{3.6}$$

It is very difficult to extrapolate to σ_L for $L>2$ from a knowledge of σ_L for $L=0$, 1, and 2, especially when these are not all that accurate, but the indications are that σ_L for $L>2$ will be quite small (Table VI). The differential cross sections $\sigma(\theta)$ would of course be more sensitive to the contributions from higher L, but we will not consider $\sigma(\theta)$.

We might note that as one goes to higher L the range of k over which Eq. (3.2) will be accurate will increase, since the long-range contribution to σ_L vanishes for k small as k^2, while the short-range contribution to σ_L vanishes for k small as k^{4L}. It must be remembered, however, that the long-range contribution to σ_L vanishes for large L as $1/L^6$.

4. SUMMARY AND DISCUSSION

Rigorous lower bounds on η_1 and η_2 as well as estimates of these phase shifts ($\tilde{\eta}_1$ and $\tilde{\eta}_2$) which include various corrections are given in Table V and also in Figs. 3 and 4 for $L=1$ and $L=2$, respectively. As discussed in Ref. 8 the estimation was a difficult task and at best only a crude one. However, the fact that the estimated values with the MP for $L=0$ and the presumably reliable results of Schwartz are in close agreement suggests that our treatment of higher angular momenta using (2.16) is fairly reliable.

The present study clarifies several interesting aspects of the applicability of the MP as well as of the e^+H scattering problem. As found in the case of zero-incident energy,[2] the effect of the target distortion during the collision is very important, presumably due to the virtual formation of positronium. This manifests itself through the extremely slow convergence in l_1. Because of this slow convergence in l_1, and furthermore because of the slow convergence in $n(>l_1)$ as indicated in Table II, the C.C.A. will in the present problem be relatively ineffective, except as a preliminary orientation. Moreover, the convergence in l_1 should be carefully studied.

The contribution from the state $l_1=1$ to $\eta(l_1;\text{MP})$, as seen from Table V, is by far the most important one, as expected, since the induced dipole potential which varies as $1/r^4$ is the leading term in the effective long-range interaction. This table also points out, in agreement with the prediction of Ref. 4, that the relative importance of the l_1 state is energy-dependent. The contribution from the $l_1=1$ state is about 90% of the total for $L=1$ and even higher for $L=2$ for $ka_0=0.1$, but drops to about 50% for $ka_0=0.7$.

It is seen from Table VI that in order to obtain an estimate of the total cross section it is necessary to have the phase shifts for at least $L=1$ and $L=2$.

The MP gives a bound on Δ, and a bound on η is obtained by solving (2.35) for η. The fractional error in η is related to the fractional error in Δ by

$$\delta\eta/\eta\approx\frac{\delta\Delta}{\Delta}\times\frac{\eta-\eta^P}{\eta}. \qquad (4.1)$$

If $|\eta^P|\gg|\eta|$ one may therefore obtain a large error in η even if the error in Δ is small.

For example, if one compares the values of $\eta_1(\text{MP})$ with $\eta_1(\text{F.Mc})$ for $ka_0=0.2$ given in Table II, one finds that the former value differs from the latter by less than 1%, while if the comparison is made for $ka_0=0.7$, the difference is nearly 8%. However, if one compares the value of Δ obtained from

$$\Delta=-ka_0\tan(\eta_1(\text{MP})-\eta_1{}^P) \qquad (4.2)$$

with

$$\Delta=-ka_0\tan(\eta_1(\text{F.Mc})-\eta_1{}^P), \qquad (4.3)$$

one finds that for both $ka_0=0.2$ and $ka_0=0.7$ the Δ value thus obtained differs by less than 1%. This example illustrates the statement made in the preceding paragraph.

The e^+H problem represents a rather unfavorable case. It should be much easier to obtain a reasonably accurate estimate of η in the e^-H problem, since η is rather close to η^P. However, in the e^-H problem one is beset by initial difficulties, of formulation and of the calculation of the various static quantities, which have their origin in the Pauli principle.[18a]

We now compare our values for the phase shifts with those estimated by different methods.[19,20] Estimates for the phase shift for $L=1$ have been obtained by Temkin[19] and by Bransden.[20] There does not appear in the literature, to the best of our knowledge, any estimate of the phase shifts for $L=2$ for us to be able to compare with our final results.

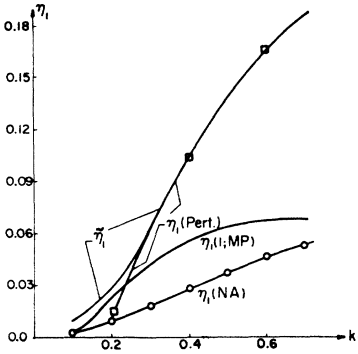

Figure 5

FIG. 5. η_1 in radians, in various approximations, including the nonadiabatic approximation of Ref. 19, η_1(NA), and the perturbation approximation of Ref. 20, η_1(Pert.). η_1 (1; MP) and $\tilde{\eta}_1$ are defined in the caption for Fig. 3. η_1(NA) includes only $l_1=0$ and $l_1=1$ contributions and should therefore be compared with η_1(1; MP). η_1(Pert.) should be compared with $\tilde{\eta}_1$.

Bransden, who uses a perturbation method and allows for the effect of the ground state of virtual positronium in his function, obtains values for the phase shifts for $L=0$ which are off by a factor of 2 and 3, and even have the wrong sign as compared with the best known values obtained with the MP[8] and by Schwartz,[3] as shown in Table VII, who also allows for the effect of virtual positronium in his trial function. This indicates that at least for $L=0$ Bransden's method is somewhat unreliable, unless one assumes that the disagreement is due to the fact that Bransden did not use higher positronium states in his perturbation method. The nonadiabatic method used by Temkin is roughly analogous to our inclusion in the trial function of $l_1=0$ and $l_1=1$. It is seen from Table VIII and Fig. 5 that the phase shifts with the nonadiabatic method for $L=1$ are much smaller than the results obtained with the MP. Since the phase shifts obtained with the MP are rigorous lower bounds on the true phase shift the nonadiabatic method does not seem to give useful results, unless one assumes that the disagreement is due to the fact that the latter method did not include a sufficient number of linear parameters. The phase shifts obtained by Bransden for $L=1$ are much higher than those obtained by Temkin, but for $ka_0=0.2$ it is lower than our rigorous lower

TABLE VII. Estimates of the $L=0$ phase shift obtained variationally (Var.), by extrapolation of the minimum principle (MP) results, and by perturbation (Pert.) theory.

ka_0	Var.[a]	MP[b]	Pert.[c]
0.1	0.151		0.044
0.2	0.188	0.182(11)	0.057
0.3	0.168		0.022
0.4	0.120	0.119(13)	−0.051
0.5	0.062		−0.144
0.6	0.007	0.009(12)	−0.236
0.7	−0.054		−0.299

[a] See Ref. 3. [b] See Ref. 8. [c] See Ref. 20.

[18a] *Note added in proof.* As expected, the e^-H calculations do give much more accurate results for a given number of parameters than do the e^+H calculations. Results obtained by Aronson, Henry, Kleinman, Hahn, and Spruch (to be published) agree with those of Schwartz[3] to four significant figures.

[19] A. Temkin, Proc. Phys. Soc. (London) **A80**, 1297 (1962).

[20] B. H. Bransden, Proc. Phys. Soc. (London) **79**, 190 (1962).

TABLE VIII. Estimates of η_1 in various approximations. The second and third columns represent the all s+all p phase shift as calculated by the nonadiabatic (NA) approach and by the MP. The last three columns are estimates of the full $L=1$ phase shift η_1 as calculated by perturbation (Pert.) theory, variationally (Var.), and from the MP. The numbers in parentheses give the uncertainty in the last digits.

	all s+all p		Full phase shift		
ka_0	NA[a]	MP[b]	Pert.[c]	Var.[d]	$\bar{\eta}_1$[e]
0.1	0.002	0.004		0.009(1)	0.009(0)
0.2	0.009	0.024	0.016	0.033(1)	0.032(1)
0.3	0.018	0.041		0.065(1)	0.066(4)
0.4	0.028	0.056	0.104	0.102(1)	0.106(8)
0.5	0.037	0.064		0.132(1)	0.137(12)
0.6	0.046	0.067	0.167	0.156(2)	0.168(17)
0.7	0.053	0.068		0.178(3)	0.186(20)

[a] See Ref. 19.
[b] Present rigorous lower bounds.
[c] See Ref. 20.
[d] See Ref. 12.
[e] Estimate based on present rigorous lower bounds.

bounds and is therefore wrong. Bransden's values can be expected to be more reliable for higher energies and for higher values of L, since perturbation theory is then more trustworthy. In particular, since he includes a positronium wave-function component in his trial function, his results might be expected to be reliable for $L=1$ and even more so for $L=2$ for energies near the pickup threshold, and his results for $ka_0=0.4$ and 0.6 are in fact very close to our estimated values. (See Fig. 5 and Table VIII.)

The very recent $L=1$ calculation by Armstead[12] is based on Schwartz's modification of the Kohn variational scheme and gives results for the phase shift after regions of good convergence have been obtained which are rather close to our results as shown in Table VIII.

We have used the MP to calculate the phase shifts for the single channel e^+H scattering for higher partial waves. The purpose has been not merely to obtain accurate results, but to study the validity as well as the applicability of the principle. From this study we have reached the following general conclusions:

(1) The MP is very helpful in evaluating the results obtained by various approximation methods, especially when the results obtained with them lie below the rigorous lower bounds.

(2) We have found no anomalies and infinities[16] occurring in $ka_0 \cot(\eta_L-\theta)$, contrary to the usual variational principles of the Kohn, Hulthén, or Schwinger type. The value of $ka_0 \cot(\eta_L-\theta)$ converges, as the trial function is improved, *monotonically*, and thus enables us, for example, to search for better parameters.

(3) For this particular problem, the expansion of the function in terms of eigenfunctions of the total angular momenta does not converge very rapidly and it is very difficult to obtain better than perhaps 5% accuracy with the form of the trial function given by (2.16) when only up to 60 linear parameters are used. It should be stressed that the poor accuracy is not the fault of the method but is due to the particular expansion we used for convenience of numerical calculation.

(4) It would be extremely desirable to have a method that would enable one to calculate the opposite bound,[21] even if only crudely, so that one gets a rough idea of how far the lower bound is from the true value. This is, of course, true for the bound-state problem as well.

(5) There are various possibilities for eliminating the need for obtaining G^P explicitly. The progress that has been made along these lines, and the associated advantages and disadvantages, are reviewed briefly in Ref. 8.

ACKNOWLEDGMENT

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APPENDIX A: THE RATIOS OF THE CONTRIBUTIONS OF DIFFERENT VIRTUAL EXCITATIONS

For the low-energy scattering of a positron by a H atom—more generally, of a charged particle by a neutral polarizable system with zero-orbital angular momentum—the H atom will be virtually excited and will thereby acquire various multipole moments. We will be concerned here with the long-range effects of these induced multipole moments. The most significant effect will be that due to the virtually excited p states of the atom ($l_1=1$), which give rise to an induced dipole moment. The p states can be excited because the interaction with the uniform component of the electric field generated by the positron contains a $\cos\theta$ factor. The uniform component and therefore the amplitude of the p-state excitation is proportional to $1/r_2^2$. Since the potential of a point charge in the field of a dipole falls off as $1/r_2^2$, we obtain as is well known a long-range interaction which is proportional to $-\alpha_1/r_2^4$, where α_1 is the electric dipole polarizability of the H atom. In precisely the same way, the excitation of electronic d states by the inhomogeneous field generated by the positron will be found to fall off as $-\alpha_2/r_2^6$, where α_2 is the electric-quadrupole polarizability of the H atom. We will always be concerned only with the leading term.

The electron and the positron have initial angular momentum values of 0 and L, respectively. During the

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[21] L. Spruch, in Ninth Yugoslav Meeting of Physicists on the Few Nucleon Problem, Hercegnovi, July 1964, Yugoslavian Atomic Energy Commission, edited by M. Cerineo (to be published); R. Sugar and R. Blankenbecler, Phys. Rev. **136**, B472 (1964); Y. Hahn, Phys. Rev. **139**, B212 (1965).

interaction, while exciting the electron to a state of angular momentum l_1, the positron will itself be excited to a state of angular momentum l_2. For fixed values of L and of l_1, there are $N(l_1,L)$ values of l_2, where

$$\begin{aligned} N(l_1,L) &= L+1 \quad \text{for} \quad l_1 \geq L \\ &= l_1+1 \quad \text{for} \quad l_1 \leq L. \end{aligned} \tag{A1}$$

For the long-range effects under consideration, the quantity Δ which is the primary concern of the present article can be decomposed as

$$\Delta = \sum_{l_1=1}^{\infty} \Delta^{(l_1)},$$

where $\Delta^{(l_1)}$ represents the contribution due to virtual excitation of electron states of angular momentum l_1. (s states only arise due to short-range effects, since $1/r_2 - 1/r_{12}$ has no long range $l_1=0$ component.) $\Delta^{(l_1)}$ can in turn be decomposed into $N(l_1,L)$ components associated with the different possible values of l_2. Our objective here is to calculate the *ratios* of these $N(l_1,L)$ contributions. Aside from its intrinsic theoretical interest, these ratios will serve as a partial check on our MP computation for $L>0$.

The point is that phase shifts behave as $\eta_L \propto k^{2L+1}$ for short-range potentials, as $\eta_L \propto k^2$ for potentials which behave asymptotically as $1/r^4$, and as $\eta_L \propto k^4$ for potentials which behave asymptotically as $1/r^6$. For sufficiently low energies, therefore, there are values of L, l_1, and l_2 for which short-range effects are irrelevant. This is never the case for $L=0$. For $L \geq 1$, the $l_1=1$ contribution dominates and can be predicted from a knowledge of α_1; even more reliably, since errors will probably tend to cancel, and without a knowledge of α_1, we can predict the ratio of the $l_1=1$, $l_2=L-1$ to the $l_1=1$, $l_2=L+1$ contribution. If we restrict ourselves to $L \geq 2$, the $l_1=1$ contribution must of course continue to dominate, but now even the $l_1=2$ contribution has a lower energy dependence than, and is therefore dominant over, the short-range effects. Thus, even though the contribution is smaller than that from $l_1=1$, we can for $L \geq 2$ predict the $l_1=2$ contribution from a knowledge of α_2, and more reliably and without a knowledge of α_2, we can predict the ratio of the $l_1=2$, $l_2=L-2$ to the $l_1=2$, $l_2=L$ to the $l_1=2$, $l_2=L+2$ contributions.

The ratio of virtual excitations will be obtained from an analysis of the expression[7]

$$\Delta = (2ma_0/\hbar^2)(P\Psi^P, PHQ\Psi), \tag{A2}$$

where $P\Psi^P$ is given by (2.4) and $Q\Psi$ is given by[7]

$$Q\Psi = \{Q(E-H-HP[P(E-H)P]^{-1}PH)Q\}^{-1}QHP\Psi^P. \tag{A3}$$

Substituting (A3) into (A2) we have

$$\begin{aligned} \Delta = (2ma_0/\hbar^2)(P\Psi^P, PHQ[Q(E-H \\ -HP[P(E-H)P]^{-1}PH)Q]^{-1}QHP\Psi^P). \end{aligned} \tag{A4}$$

We are interested in those contributions in the integral in (A4) which come from very large values of r_2. Since the term containing $[P(E-H)P]^{-1}$ is a potential term which vanishes for large separation as $1/r_2^4$, and thus gives contributions to the optical potential which vanish as $1/r_2^8$, we neglect it in the following consideration; then (A4) may be approximated for present purposes by

$$\Delta \approx (2ma_0/\hbar^2)(P\Psi^P, PHQ[Q(E-H)Q]^{-1}QHP\Psi^P). \tag{A5}$$

While the inverse operator given in (A5) is perfectly well defined, it is not yet in a useful form. Using the standard relation $1/A = 1/B + (1/B)(B-A)(1/A)$,

$$\begin{aligned} &[Q(E-H)Q]^{-1} \\ &\quad = [Q(E_{T0}-H_T)Q]^{-1} + [Q(E_{T0}-H_T)Q]^{-1} \\ &\qquad\qquad \times Q(T+V-E')Q[Q(E-H)Q]^{-1} \\ &\quad = [Q(E_{T0}-H_T)Q]^{-1} + [Q(E_{T0}-H_T)Q]^{-1} \\ &\qquad \times Q(T+V-E')Q[Q(E_{T0}-H_T)Q]^{-1} + \cdots \\ &\qquad\qquad\qquad = G_0^Q + G_1^Q + \cdots, \end{aligned} \tag{A6}$$

and note that the asymptotic contribution to (A5) involving the G_1^Q term has been shown[22,23] to fall off faster for any l_1 than the G_0^Q term contribution. Since for each l_1 we are only interested in the leading term in the interaction potential at large r_2, we can write

$$\begin{aligned} &[Q(E-H)Q]^{-1} \\ &\quad \approx [Q(E_{T0}-H_T)Q]^{-1} \\ &\quad = \sum_{n,l_1,l_2}{}' |R_{nl_1}(r_1)\mathcal{Y}_{Ll_1l_2}(\Omega_{12})\rangle \\ &\qquad\qquad \times [E_{T0}-E_{Tn}]^{-1}\langle R_{nl_1}(r_1)\mathcal{Y}_{Ll_1l_2}(\Omega_{12})|. \end{aligned} \tag{A7}$$

Using (A7), Eq. (A5) may be written in the case for which the dominant contribution comes from large r_2 as

$$\begin{aligned} \Delta \approx 2e^2 \sum_{n,l_1,l_2,\lambda,\nu}{}' [E_{T0}-E_{Tn}]^{-1} I(\lambda,n,l_1,l_2) I^*(\nu,n,l_1,l_2) \\ \times \int [u_L^P(r_2)]^2 r_2^{-\lambda-\nu-2} dr_2, \end{aligned} \tag{A8}$$

where the prime indicates that $n=1$, $\lambda=1$, and $\nu=1$ are excluded, where

$$I(\lambda,n,l_1,l_2) = f_\lambda(l_1,l_2,O,L;L) \int R_{10}(r_1) r_1^{\lambda+2} R_{nl_1}(r_1) dr_1,$$

and where f_λ is defined by Eq. (2.23). If we use Eqs. (2.23), (2.26), and (2.27), Δ may be written as

$$\Delta \approx \sum_{l_1=1}^{\infty} \Delta^{(l_1)}, \tag{A9}$$

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[22] M. H. Mittleman and K. M. Watson, Phys. Rev. **113**, 198 (1959); M. H. Mittleman, B. A. Lipmann, and K. M. Watson, Phys. Rev. **116**, 920 (1959); M. H. Mittleman, Ann. Phys. (N. Y.) **14**, 94 (1961).

[23] C. J. Kleinman, Y. Hahn, and L. Spruch (to be published).

where

$$\Delta^{(l_1)}=-2\sum_{l_2}|f_{l_1}(0,L,l_1,l_2;L)|^2\alpha_{l_1}\times\int(u_L{}^P)^2r_2{}^{-2l_2-2}dr_2,\quad\text{(A10)}$$

where

$$\alpha_{l_1}=-e^2\sum_n{}'\left|\int R_{10}(r_1)r_1{}^{l_1+2}R_{n\,l_1}(r_1)dr_1\right|^2\times(E_{T0}-E_{Tn})^{-1},\quad\text{(A11)}$$

and where $N(l_1,L)$ values of l_2 contribute to $\Delta^{(l_1)}$.

In general α_{l_1} is not known, but that does not matter for the present analysis since it is independent of l_2. The essence of the argument is that the radial integrals are the same whether the positron jumps into one or another of its possible values of l_2 and the ratio is then determined completely by a knowledge of the various angular integrations involved. It should be noted that α_1 and α_2 are the dipole- and quadrupole-electric polarizability of the atom, respectively.

We find for $l_1=1$ and $L>0$,

$$\Delta^{(1)}=-\alpha_1[|f_1(0,L,1,L-1;L)|^2+|f_1(0,L,1,L+1;L)|^2]\int(u_L{}^P)^2r_2{}^{-4}dr_2$$
$$=-\alpha_1\left[\frac{L}{3(2L+1)}+\frac{L+1}{3(2L+1)}\right]\times\int[u_L{}^P(r_2)]^2r_2{}^{-4}dr_2\quad\text{(A12)}$$

so that the ratios of the $l_2=L-1$ to $l_2=L+1$ contribution to $\Delta^{(1)}$ is given by

$$\Delta_{l_2=L-1}{}^{(1)}:\Delta_{l_2=L+1}{}^{(1)}=L:L+1,\quad\text{for}\quad L\neq 0.\quad\text{(A13)}$$

We also have, for $l_1=2$, and $L>1$,

$$\Delta^{(2)}=-\alpha_2[|f_2(0,L,2,L-2;L)|^2+|f_2(0,L,2,L;L|^2+|f_2(0,L,2,L+2;L)|^2]\int(u_L{}^P)^2r_2{}^{-6}dr_2$$

from which we obtain the ratios

$$\Delta_{l_2=0}{}^{(2)}:\Delta_{l_2=2}{}^{(2)}:\Delta_{l_2=4}{}^{(2)}=7:10:18,\quad\text{for}\quad L=2.\quad\text{(A14)}$$

The theoretical results and the results obtained with the MP are in quite good agreement as shown in Table IV. Since the ratios of the Δ_γ's corresponding to a given $\Delta^{(l_1)}$ are independent of α_{l_1}, in the actual calculation we use for convenience single eigenstates of the target with lowest n values, i.e., $n=l_1+1$.

APPENDIX B: MATRIX ELEMENTS FOR $L=1$

In this Appendix some details of the calculation for a total angular momentum $L=1$ will be presented. For $L=1$ where the trial function includes values for $l_1=0$ through $l_1=3$, the values for l_2 that have to be considered are given in Table I, together with the labeling index $\gamma=\gamma(l_1,l_2;1)$. Thus we have

$$Q\Psi_{1t}=\sum_i\sum_{\gamma=0}^{6}c_{i\gamma}Q\Psi_{i\gamma},\quad\text{(B1)}$$

where the index i indicates that, for each value of γ, more than one set of values of b and of d may be considered and where

$$a_0{}^{5/2}x_1x_2Q\Psi_{i\gamma}=\omega_{i\gamma}(x_1)\chi_{i\gamma}(x_2)\mathcal{Y}_{i\gamma},\quad\text{(B2)}$$

with $\omega_{i\gamma}$ and $\chi_{i\gamma}$ given by (2.17a) and (2.17b), respectively. Thus for any i we have to calculate $7N$'s and $28K$'s.

In all of the N's, defined by (2.37), there appear integrals of the type

$$Z(m,n,b;x)=\int_0^\infty dx'(x_</x_>)^m(x'^n/x_>)\exp(-bx').\quad\text{(B3)}$$

We have

$$Z(m,n,b;x)=\frac{(n+m)!}{b^{n+m+1}}\times\frac{1}{x^{m+1}}\left[1-\exp(-bx)\left(\frac{(bx)^{n+m}}{(n+m)!}+\frac{(bx)^{n+m-1}}{(n+m-1)!}+\cdots+\frac{bx}{1!}+1\right)\right]+\frac{x^m(n-m-1)}{b^{n-m}}\exp(-bx)$$
$$\times\left(\frac{(bx)^{n-m-1}}{(n-m-1)!}+\frac{(bx)^{n-m-2}}{(n-m-2)!}+\cdots+\frac{bx}{1!}+1\right).\quad\text{(B4)}$$

If we define $U_p(z)$ as

$$U_p(z)=-2\sum_{l_2}f_{l_1}(l_1,l_2,0,L;L)Z(m,n,b;z),\quad\text{(B5)}$$

Eq. (2.37) may be written as

$$a_0N_p=\int dz\chi_p(z)u^P(z)U_p(z).\quad\text{(B6)}$$

Equation (2.39) can be written as

$$K_{a,i\gamma j\gamma}=(2l_2+2)!(2l_1+2)!D_{i\gamma,j\gamma}{}^{-(2l_2+3)}B_{i\gamma,j\gamma}{}^{-(2l_1+3)}\times([D_{i\gamma,j\gamma}/(l_2+1)]+d_{i\gamma}d_{j\gamma}-[B_{i\gamma,j\gamma}/(l_1+1)]+b_{i\gamma}b_{j\gamma}-\mathcal{E}),\quad\text{(B7)}$$

where

$$D_{i\gamma,j\gamma}=d_{i\gamma}+d_{j\gamma}\quad\text{and}\quad B_{i\gamma,j\gamma}=b_{i\gamma}+b_{j\gamma}.\quad\text{(B8)}$$

Equation (B7) does not hold for $K_{a,i0j0}$ because of the special form Eq. (2.17a) assumes for $\gamma=0$.

In Eq. (2.40) there appear integrals of the form

$$I(m,n,B;s,D)=\int dx_2\, x_2^s \exp(-Dx_2)\int dx_1\, x_1^n \times\exp(-Bx_1)(x_<^m/x_>^{m+1})\,; \quad \text{(B9)}$$

such integrals can be evaluated by writing I as

$$I=(B+D)^{-n-s}[J(m,n,B;s,D)+J(m,s,D;n,B)]\,, \quad \text{(B10)}$$

where

$$J(m,n,B;s,D)=\frac{(s-m-1)!}{D}\times\sum_{t=0}^{s-m-1}\frac{(n+s-1-t)!}{(s-m-1-t)!}\left(\frac{B+D}{D}\right)^t.$$

Using (B10) $K_{b,pq}$ can be written as

$$K_{b,pq}=-2\sum_{\lambda} f_\lambda(l_1,l_2,l_1',l_2';L)I(\cdots)\,. \quad \text{(B11)}$$

Using Eq. (B5) $K_{c,pq}$ as given by Eq. (2.41) can be written as

$$(-ka_0^3)K_{c,i\gamma j\rho}=\int_0^\infty dz\,\chi_{i\gamma}(z)U_{i\gamma}(z)\left\{\int_0^\infty dz'\,U_{j\rho}(z')\chi_{j\rho}(z')\times[u_{\text{reg}}^P(z_<)u_{\text{irreg}}^P(z_>)-\cot(\eta^P-\theta)u_{\text{reg}}^P(z)u_{\text{irreg}}^P(z')]\right\}. \quad \text{(B12)}$$

Thus, the prescription to calculate $N_{i\gamma}$ and $K_{c,i\gamma j\rho}$ involves the $U_{i\gamma}$. We present the matrix elements for $\gamma=0$ and 1 only.

$$\gamma=0 \qquad l_1=0,\quad l_2=1$$

$$U_{i0}(z)=4a_iZ(0,2,2;z)-4Z(0,2,A_{i0};z)\,.$$

$$\begin{aligned}K_{i0j0}=2\cdot4!D_{i0,j0}^{-5}\{&[B_{i0,j0}^{-3}-8(A_{i0}A_{j0})^{-3}]\\&\times(\tfrac{1}{2}D_{i0,j0}+d_{i0}d_{j0}-\mathcal{E})-B_{i0,j0}^{-3}(B_{i0,j0}-b_{i0}b_{j0})\\&+8(A_{i0}A_{j0})^{-3}\}+2a_iI(0,2,A_{j0};4,D_{i0,j0})\\&+2a_jI(0,2,A_{i0};4,D_{i0,j0})-2a_ia_jI(0,2,2;4,D_{i0,j0})\\&-2I(0,2,B_{i0,j0};4,D_{i0,j0})+K_{c,i0j0}\,.\end{aligned}$$

$$\gamma=1 \qquad l_1=1,\quad l_2=0$$

$$U_{i1}(z)=-\tfrac{4}{3}Z(1,3,A_{i1};z)\,.$$

$$\begin{aligned}K_{i0j1}=\tfrac{2}{3}[&a_iI(1,3,A_{j1};3,D_{i0,j1})\\&-I(1,3,B_{i0,j1};3,D_{i0,j1})]+K_{c,i0j1}\,.\end{aligned}$$

$$\begin{aligned}K_{i1j1}=2\cdot4!D_{i1,j1}^{-3}B_{i1,j1}^{-5}(&D_{i1,j1}+d_{i1}d_{j1}\\&-\tfrac{1}{2}B_{i1,j1}+b_{i1}b_{j1}-\mathcal{E})\\&-2I(0,4,B_{i1,j1};2,D_{i1,j1})+K_{c,i1j1}\,,\end{aligned}$$

where Z, I, and $K_{c,i\gamma j\rho}$ are defined by (B4), (B10), and by (B12), respectively, and where

$$\left.\begin{aligned}A_{i\gamma}=b_{i\gamma}+1\,,\quad A_{j\rho}=b_{j\rho}+1\,,\\a_i=8A_{i0}^{-3}\,,\quad a_j=8A_{j0}^{-3}\,,\end{aligned}\right\} \quad \text{(B13)}$$

and

$$\mathcal{E}=-1+(ka_0)^2.$$

The values of the $b_{i\gamma}$ and of the $d_{i\gamma}$ used for each γ, and the matrix elements for $1\leq\gamma\leq6$ for $L=1$ and $0\leq\gamma\leq5$ for $L=2$ are given in the thesis and will be supplied upon request.