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Nonadiabatic Theory of Electron-Hydrogen Scattering

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A rigorous theory of the s-wave elastic scattering of electrons from hydrogen is presented. The Schrödinger equation is reduced to an infinite set of coupled, two-dimensional partial differential equations. A zeroth order scattering problem is defined by neglecting the coupling terms of the first equation. An exact relation is derived between the phase shift of this zeroth order problem and the true phase shift. The difference between these is contained in a rapidly convergent series whose terms correspond adiabatically to multipole distortions of the hydrogen by the incoming electron. The physical significance of the zeroth order problem is discussed, and its recognition is considered basic to the understanding of the scattering problem. The exchange approximation for s-wave scattering is shown to be a variational approximation of the zeroth order problem. A perturbation theory is introduced to calculate the higher order corrections. The dipole correction has an increasingly important quantitative effect in the limit of zero energy. The effect of the long-range part of this correction on the scattering length can be expressed by a formula in terms of inverse powers of a long-range parameter R. Phase shifts for both singlet and triplet scattering are calculated, including up to quadrupole terms. The convergence is such that this number of terms should yield better than four-place accuracy. Uncertainties in our calculated values decrease the accuracy to approximately three significant figures.

I. INTRODUCTION[1]

The elastic scattering of electrons from atomic hydrogen is the most fundamental three-body scattering problem of quantum mechanics. Nevertheless, the process of theoretical understanding has been slow and is still not complete. Specifically, the lack of a real quantitative understanding of this problem, as compared with its counterpart, the ground state of helium problem, can be traced to two causes. The first was the lack of a minimum principle, which guarantees that not only is a certain quantity variational in character, but more important that it is greater than (or less than) the exact quantity one wants to evaluate. The lack of a minimum principle has recently been overcome by Rosenberg, Spruch, and O'Malley, who have derived minimum principles for the scattering length[2] and who are attempting to generalize the procedure to include phase shifts as well.[3] The second aspect of scattering problems which has slowed the process of quantitative understanding is simply the fact that the scattering parameters are more sensitive functions of the wave function than, say, the ground-state energy. The sensitivity may be illustrated in the case of the singlet scattering of electrons by hydrogen, where there is known to be a singlet bound state of the H^- ion with a binding energy of 14.460 ev. The electron affinity, ϵ, is defined as the difference between this energy and that of a hydrogen atom and a free electron. Clearly, this is the quantity of physical significance, for only when it is negative is the H^- bound. The electron affinity, being a small difference between two large numbers, is obviously sensitive to deviations in one of the large numbers. An approximation which undershoots the total energy by 6% predicts no binding. The fact that the H^- wave function corresponds to a barely bound system means that it must be related to the low-energy $e-H$ scattering wave function. This relationship is expressed by the approximate formula,[4]

$$|\epsilon|^{\frac{1}{2}}=1/a+\tfrac{1}{2}r_0|\epsilon|,$$

which shows likewise that the effective-range parameters, a and r_0, are also sensitive functions of the wave function.

The sensitivity of the scattering parameters, i.e., the phase shifts, to the wave function manifests itself in another way. Suppose, in considering a scattering problem, one attempts to replace the interaction of the incident particle with the (many-body) target by an equivalent one-body potential. In the bound-state problem it is known that the Hartree or Hartree-Fock method leads to just such an equivalent potential. In the case of scattering of a particle from a compound system consisting of particles *different* from the incoming particle, Mittleman and Watson[5] have developed formal expressions for just such a potential, and Mittleman[6] has modified the approach to be applicable to the scattering of electrons from hydrogen. The practical difficulty with the equivalent potential is that it is effectively a series expansion in which the derivation of successive terms is a major calculational task, particularly for the in-close behavior of the potential, and in which the physical meaning of successive terms becomes increasingly obscure. In addition, the potentials become

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[1] A sketch of this method has been published: A. Temkin, Phys. Rev. Letters **4**, 566 (1960).

[2] L. Rosenberg, L. Spruch, and T. O'Malley, Phys. Rev. **119**, 164 (1960).

[3] L. Rosenberg and L. Spruch, Phys. Rev. **121**, 1720 (1960).

[4] S. Borowitz and H. Greenberg, Phys. Rev. **108**, 716 (1957). The effective-range formalism for the $e-H$ problem has been effectively exploited by T. Ohmura, Y. Hara, and T. Yamanouchi, Progr. Theoret. Phys. (Kyoto) **20**, 82 (1958) and T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960).

[5] M. Mittleman and K. Watson, Phys. Rev. **113**, 198 (1959).

[6] M. Mittleman, Ann. Phys. **14**, 94 (1961). A nonrigorous potential applicable to electron-atom scattering generally is contained in B. Lippmann, M. Mittleman, and K. Watson, Phys. Rev. **116**, 920 (1959).

quite nonlocal in character and appear to present considerable difficulties for numerical solution.[7]

The difficulty of evaluating a potential valid over all space is symptomatic of the essentially non-two-body character of the scattering problem. The main idea of the method that we shall present here is that the correct zeroth order problem is a three-body problem. However, given the basic three-body problem, there are a variety of ways of handling it. *Thereafter*, the corrections are separable in the first approximation. The method we shall present is an extension of the method of Luke, Meyerott, and Clendenin.[8] The chief formula is (3.5) which relates the zeroth-order phase shift δ_0 with the exact s-wave phase shift δ. The main property of the terms on the right-hand side (rhs) of (3.5) is that they constitute a rapidly convergent series. They also have a natural physical interpretation as long-range polarization effects. The quantitative importance of the lower of these terms is basically an expression of the increased importance of polarization in (most) scattering problems as opposed to (most) ground-state energy problems. The polarization terms constitute the part of the wave function from which the extra sensitivity of the scattering parameters stems. Yet the main contribution of these functions comes from the (adiabatic) region where the functions are separable. The nonadiabatic method, however, projects equations for these functions over all space; one can employ various devices to get reasonable estimates of the contributions of these functions from the nonadiabatic region even without solving the associated partial differential equations. This will be the subject of the succeeding sections, and we conclude with the evaluation of fairly accurate electron-hydrogen phase shifts, and, more important, with a reliable estimate of the error.

II. DECOMPOSITION OF THE s-WAVE EQUATION

The s-wave scattering of electrons from hydrogen is described by the Schrödinger equation of zero total angular momentum for two electrons in the field of a singly charged nucleus (assumed infinitely heavy). Such an equation can be reduced to a three-dimensional partial differential equation which can be written[9]

$$\left\{-\frac{1}{r_1}\frac{\partial^2 r_1}{\partial r_1^2}-\frac{1}{r_2}\frac{\partial^2 r_2}{\partial r_2^2}-\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right.$$
$$\left.-\frac{2}{r_1}-\frac{2}{r_2}+\frac{2}{r_{12}}-E\right\}\Psi(r_1,r_2,\theta_{12})=0. \quad (2.1)$$

(Our units are energies in rydbergs, lengths in Bohr radii.) The fact that the s-wave equation can be reduced to a single three-dimensional equation is the main mathematical reason that it is susceptible to a highly quantitative treatment.

Taking advantage of the fact that the Legendre polynomials, $P_l(\cos\theta)$, are eigenfunctions of the angular dependent operator in the above equation:

$$\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}P_l(\cos\theta_{12})$$
$$=-l(l+1)P_l(\cos\theta_{12}), \quad (2.2)$$

we expand the wave function

$$\Psi(r_1,r_2,\theta_{12})=\frac{1}{r_1r_2}\sum_{l=0}^{\infty}(2l+1)^{\frac{1}{2}}\Phi_l(r_1r_2)P_l(\cos\theta_{12}). \quad (2.3)$$

Substitution into (2.1) then gives an infinite set of coupled equations

$$\left\{\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}-l(l+1)(r_1^{-2}+r_2^{-2})+E+\frac{2}{r_1}\right.$$
$$\left.+\frac{2}{r_2}-M_{ll}\right\}\Phi_l(r_1r_2)=\sum_{m=0}^{\infty}{}'M_{lm}\Phi_m(r_1r_2), \quad (2.4)$$

where in the region $r_1>r_2$

$$M_{lm}=(2l+1)^{\frac{1}{2}}(2m+1)^{\frac{1}{2}}\sum_{n=0}^{l+m}\frac{r_2^{\,n}}{r_1^{\,n+1}}$$
$$\times\int_0^{\pi}P_l(\cos\theta)P_m(\cos\theta)P_n(\cos\theta)\sin\theta d\theta. \quad (2.5)$$

Under exchange, $\mathbf{r}_1\rightleftarrows\mathbf{r}_2$, the three coordinates of the s-wave problem transform according to $r_1\rightleftarrows r_2$, $\theta_{12}\rightleftarrows+\theta_{12}$. Thus there exist singlet and triplet solutions which have the property $\Psi(r_1,r_2,\theta_{12})=\pm\Psi(r_2,r_1,\theta_{12})$, respectively. In terms of the expansion function Φ_l this implies (as a necessary and sufficient condition) that

$$\Phi_l(r_1r_2)=\pm\Phi_l(r_2r_1).$$

The symmetry of the operator in curly brackets in (2.1) further implies that the problem can be solved completely in the region $r_1\geq r_2$ by imposing the additional boundary conditions

$$\begin{aligned}\Phi_l(r_1r_2)|_{r_1=r_2}&=0, \quad \text{triplet}\\ (\partial/\partial n)\Phi_l(r_1r_2)|_{r_1=r_2}&=0, \quad \text{singlet}\end{aligned} \quad (2.6)$$

where $\partial/\partial n$ means the normal derivative. Because of the r_1r_2 factor in (2.3), we have in both cases

$$\Phi_l(r_10)=0. \quad (2.7)$$

We are restricting ourselves to the description of scattering below the threshold for inelastic scattering,

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[7] M. Mittleman (private communication).

[8] P. Luke, R. Meyerott, W. Clendenin, Phys. Rev. **85**, 401 (1952). The idea for this work is due to G. Breit. I am indebted to John W. Cooper for having brought the paper of LMC to my attention.

[9] P. M. Morse and H. Feshbach, *Method of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York 1953), p. 1725.

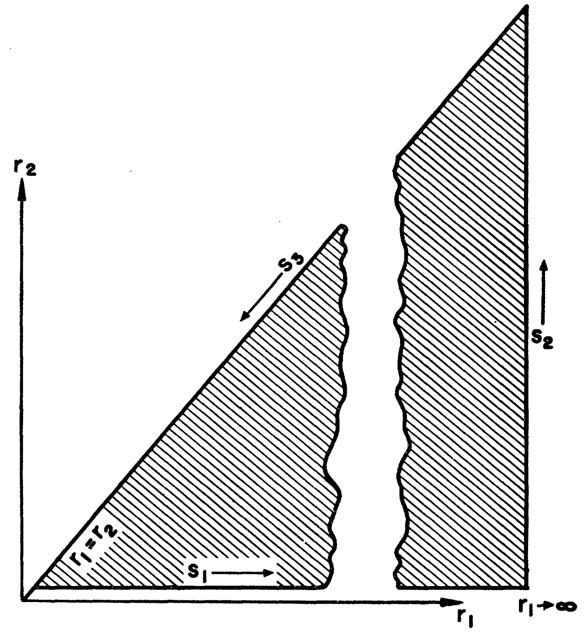

FIG. 1. The $r_1>r_2$ triangle, to which the whole mathematical problem is restricted.

thus we must also have

$$\begin{aligned}&\lim_{r_1\to\infty}\Phi_0(r_1r_2)=\sin(kr_1+\delta)R_{1s}(r_2),\\&\lim_{r_1\to\infty}\Phi_l(r_1r_2)=0,\quad l>0.\end{aligned}\tag{2.8}$$

Here k is the momentum of the scattered electron and is related to the energy by

$$E=-1+k^2.$$

$R_{1s}(r)$ is r times the (normalized) ground-state radial function of hydrogen.

The s-wave phase shifts, δ, are then completely specified by the coupled set of Eqs. (2.4) subject to the boundary conditions (2.6)–(2.8).

Clearly one must solve such a set of equations in some approximate manner. What we would like to give in the sequel is a basis for such a method of successive approximations. The virtue of the method of approximation is that there is obvious physical significance in each stage and that one can readily establish both physical as well as mathematical reasons for the rapid convergence of the series. A central role in this scheme is the zeroth order approximation, which we shall now consider.

III. THE ZEROTH ORDER APPROXIMATION AND THE MULTIPOLE EXPANSION

Noting that

$$M_{0m}=\frac{2}{(2m+1)^{\frac{1}{2}}}\frac{r_2^m}{r_1^{m+1}},\tag{3.1}$$

let us write the equation for $\Phi_0(r_1,r_2)$ explicitly:

$$\left(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+E+\frac{2}{r_2}\right)\Phi_0(r_1r_2)=\sum_{m=1}^{\infty}\frac{2}{(2m+1)^{\frac{1}{2}}}\frac{r_2^m}{r_1^{m+1}}\Phi_m.\tag{3.2}$$

It is natural to attempt to approximate this equation by neglecting the right-hand side. Consider

$$\left(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+E+\frac{2}{r_2}\right)\Phi_0^{(0)}(r_1r_2)=0,\tag{3.3}$$

subject to the boundary conditions (2.6) and (2.7) for $\Phi_0^{(0)}$, and with the asymptotic form

$$\lim_{r_1\to\infty}\Phi_0^{(0)}(r_1r_2)=\sin(kr_1+\delta_0)R_{1s}(r_2).\tag{3.4}$$

It is important to realize that, although the right hand side of (3.4) is an exact solution of (3.3), δ_0 is *not* arbitrary.[10]

A relation between δ_0 and δ can be established by multiplying (3.3) by Φ_0 and (3.2) by $\Phi_0^{(0)}$, subtracting and integrating over the half plane $r_2\leq r_1$; one gets

$$\int_0^\infty\int_0^{r_1}(\Phi_0\Delta_{12}\Phi_0^{(0)}-\Phi_0^{(0)}\Delta_{12}\Phi_0)dr_1dr_2=-\sum_{m=1}^{\infty}\int_0^\infty\int_0^{r_1}\Phi_0^{(0)}M_{0m}\Phi_m dr_1dr_2.$$

The operator

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

is the two-dimensional Laplacian, and using Green's theorem, we can write the left-hand side of (3.4) as

$$\int_0^\infty\int_0^{r_1}(\Phi_0\Delta_{12}\Phi_0^{(0)}-\Phi_0^{(0)}\Delta_{12}\Phi_0)dr_1dr_2=\int_s\left(\Phi_0\frac{\partial}{\partial n}\Phi_0^{(0)}-\Phi_0^{(0)}\frac{\partial}{\partial n}\Phi_0\right)ds.$$

The boundary s goes around the region $r_1>r_2$ and is thus the triangle indicated in Fig. 1. The line integral along s_1 is zero by virtue of (2.7) and its counterpart for $\Phi_0^{(0)}$. The integral along s_3 is zero via (2.6) so that we are left with only the integral along s_2. Here $\partial/\partial n=\partial/\partial r_1$, and using the asymptotic forms of Φ_0 and $\Phi_0^{(0)}$, (2.7) and (3.4), and the assumption that R_{1s} is

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[10] In the language of partial differential equations, (3.3) is an elliptic equation with Dirchlet boundary conditions along all sides for the triplet case and with Neumann conditions along s_3 in the singlet case (see Fig. 1). The boundary condition along s_2 is $\Phi_0^{(0)}(\infty,r_2)=CR_{1s}(r_2)$, where C is an arbitrary constant corresponding to the arbitrariness in normalization of $\Phi_0^{(0)}$. For a given C, the uniqueness of the solution then guarantees that δ_0 is unique (modulo 2π).

normalized, we arrive at our main formula:

$$\sin(\delta-\delta_0)=-\frac{1}{k}\sum_{m=1}^{\infty}\frac{2}{(2m+1)^{\frac{1}{2}}}\times\int_0^{\infty}dr_1\int_0^{r_1}dr_2\,\Phi_0^{(0)}\frac{r_2^{m}}{r_1^{m+1}}\Phi_m. \qquad (3.5)$$

Equation (3.3) is the zeroth order problem and δ_0 the zeroth order phase shift. It must be emphasized that in spite of the separability of (3.3) as a partial differential equation, the problem is nonseparable by virtue of the nonseparable boundary condition (2.6) for $\Phi_0^{(0)}$. The physical meaning of the equation is clear. Electron 1 comes in seeing no charge at all while the orbital electron 2 sees the whole nuclear charge. When electron 1 gets inside electron 2, it sees the whole nuclear charge and becomes the orbital electron while electron 2 goes off as the scattered particle seeing no charge. This, of course, is nothing but the shielding approximation as it applies to a scattering problem. Yet, because the position of electron 1 is correlated with the position of electron 2 which itself is variable, this is distinctly a three-body problem. It is the thesis of this paper that this rudimentary three-body problem is at the core of this scattering problem, and that attempts to reduce the problem further are either equivalent to mathematical reformulations of the problem or that they bring in dubious approximations.

It is not difficult to show that the exchange approximation,[11] which uses an ansatz Ψ_{EA} not depending on the angle θ_{12}:

$$r_1r_2\Psi_{\mathrm{EA}}=u(r_1)R_{1s}(r_2)\pm u(r_2)R_{1s}(r_1),$$

for the s-wave wave function, is in fact a variational solution of only that part of the original Schrödinger equation corresponding to (3.3). For if one considers the matrix element of the complete interaction, $+2/r_1+2/r_2-2/r_{12}$, with any (symmetric or antisymmetric) function of the form $f(r_1,r_2)$,[12] then the integral

$$\int\int f^*(r_1,r_2)\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{2}{r_{12}}\right)f(r_1,r_2)d^3r_1d^3r_2$$

$$\propto\int_0^{\infty}\int_0^{\infty}|r_1r_2f(r_1,r_2)|^2\frac{2}{r_<}dr_1dr_2$$

$$=2\int_0^{\infty}dr_1\int_0^{r_1}dr_2\,|r_1r_2f(r_1,r_2)|^2\frac{2}{r_2},$$

where we have used the (anti-) symmetry of $f(r_1,r_2)$. (Note that other terms of the Schrödinger equation will also yield matrix elements in this region multiplied by a factor 2.) We shall see in the next section that the exchange approximation yields phase shifts practically identical to δ_0.[12] As such, it is an excellent approximation of $\Phi_0^{(0)}$, yet from (3.5) we see that it neglects all the higher order corrections associated with the functions Φ_l.

One more remark is in order concerning the zeroth order problem and δ_0 in particular: there are no long-range polarization forces associated with the zeroth order problem, so that the boundary conditions associated with $\Phi_0^{(0)}$, aside from its s-wave sinusoidal behavior at infinity, are very much like a bound-state problem. This is quite different from the phase shift of the whole problem in which there are long-range polarization forces, which are, however, manifested in $\Phi_l(l>0)$. A practical consequence of this is that δ_0 considered as a function of r_1 quickly assumes its asymptotic form as is typical for a particle scattered from a short-range potential. In fact, the Hartree-Fock exchange approximation potential is an exponentially decaying one. Thus, in contrast to δ, which only slowly assumes its asymptotic form, δ_0 can truly be regarded as unvarying for large r_1. [This consideration is relevant in the derivation of (5.15).]

The physical meaning of the functions Φ_l can be gleaned from the adiabatic region (defined as the region $r_1\gg r_2$, $r_1\gg1$). In this region only the function Φ_0 fails to vanish and only the first term of M_{ll} $(=-2/r_1)$ in (2.4) need be considered. Thus, these equations reduce to

$$\left(\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}-\frac{l(l+1)}{r_2^2}+\frac{2}{r_2}-1+k^2\right)\Phi_l=\frac{2r_2^{l}}{(2l+1)^{\frac{1}{2}}}\frac{\sin(kr_1+\delta)}{r_1^{l+1}}R_{1s}(r_2). \qquad (3.6)$$

A solution of this equation, neglecting the operation $\partial^2/\partial r_1^2$ on $r_1^{-(l+1)}$ (which is also justified in this region), is

$$\Phi_l\cong\frac{-2}{(2l+1)^{\frac{1}{2}}}\frac{\sin(kr_1+\delta)}{r_1^{l+1}}e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right). \qquad (3.7)$$

These functions represent multipole distortions of the hydrogen atom caused by an electron at some distance from the atom.[13]

Having obtained the adiabatic form of Φ_l, we can now qualitatively establish the reasonably rapid convergence of (3.5). The configuration space of each double integral can be divided into roughly four regions, schematically indicated in Fig. 2. In region D, the adiabatic region, one can use the explicit forms of $\Phi_0^{(0)}$ and Φ_l to see that the contributions from that region go down rapidly as a

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[11] P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

[12] S. Geltman [Phys. Rev. **119**, 1283 (1960)] has computed variational phase shifts using wave functions, which for s waves are functions of r_1 and r_2 only. According to our analysis, his phase shifts are approximations of the zeroth order δ_0 only. K. Smith [Phys. Rev. **120**, 845 (1960)] has used the close-coupling extension of the exchange approximation including various numbers of excited s states in his wave functions. These too can only approximate δ_0.

[13] A. Dalgarno and A. Stewart, Proc. Roy. Soc. (London) **A238**, 269, 276 (1956). A. Temkin, Phys. Rev. **116**, 358 (1959).

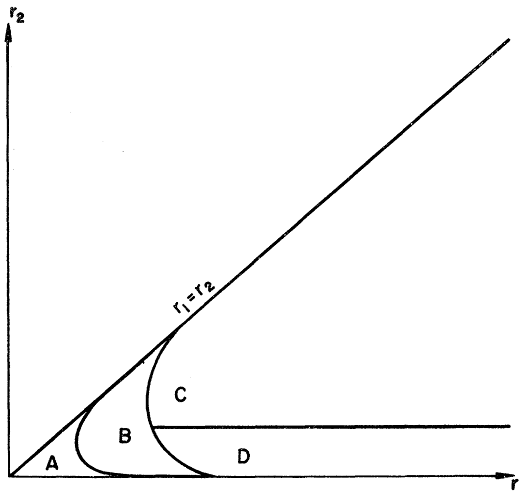

FIG. 2. The regions of configuration space which give different magnitude contributions to the multipole integrals.

function of l. In region C where $r_2 \cong r_1$ and both are large, the contribution is very small in all cases. This is because $\Phi_0^{(0)}$ and the Φ_l decay exponentially there, roughly as $\exp[-(-\frac{1}{2}E)^{\frac{1}{2}}(r_1+r_2)]$. (Note $E<-\frac{1}{4}$ for all the energies we are considering.) In region A where both r_1 and r_2 are small, the $\Phi_l(l>0)$ are necessarily small by virtue of the centrifugal barrier $-l(l+1)(1/r_1^2+1/r_2^2)$ which pushes the wave functions out from that region.[14] For intermediate values of r_1 and r_2, region B, there will be an important quantitative contribution whose convergence as a function of l stems from the gradual disappearance of the region B itself as region A merges into regions C and D.

As a function of increasing energy the multipole terms on the right-hand side of (3.5) have a decreasingly important effect on the cross section. Nevertheless the quantitative contribution of these terms becomes more difficult to calculate. This is because at the lowest energies the proportionate contribution from region D is sizeable yet the function is known there. For higher energies the proportionate contribution from region D becomes quite small.

IV. SOLUTION OF THE ZEROTH ORDER PROBLEM

It has already been emphasized that Eq. (3.3) together with the boundary conditions

$$\Phi_0^{(0)}(r_1 0)=0, \tag{4.1}$$

$$\lim_{r_1\to\infty}\Phi_0^{(0)}(r_1 r_2)=\sin(kr_1+\delta_0)R_{1s}(r_2), \tag{4.2}$$

$$\begin{aligned} \Phi_0^{(0)}(r_1 r_2)\,|_{r_1=r_2}&=0, \quad \text{triplet} \\ (\partial/\partial n)\Phi_0^{(0)}\,|_{r_1=r_2}&=0, \quad \text{singlet} \end{aligned} \tag{4.3}$$

presents a highly nonseparable problem. Nevertheless, Eq. (3.3) itself is separable, and the separable solutions can readily be written down. We shall expand the exact solution, $\Phi_0^{(0)}$, in terms of the totality of such separable solutions which can possibly enter the expansion:

$$\Phi_0^{(0)}=\sin(kr_1+\delta_0)R_{1s}(r_2) + \left(\sum{}_n+\int dp\right)C_n e^{-\kappa_n r_1}R_{ns}(r_2). \tag{4.4}$$

The sum plus integral means, as usual, that the continuum s states of hydrogen in addition to the discrete states must be included. For the discrete states

$$\kappa_n=(1-n^{-2}-k^2)^{\frac{1}{2}}, \tag{4.5}$$

and for the continuum

$$\kappa_p=(1+p^2-k^2)^{\frac{1}{2}}. \tag{4.6}$$

Since each term of (4.4) is separately a solution of (3.3), the only thing which prevents any expansion from being an exact solution is its deviation from the boundary condition (4.3). [Note that (4.1) and (4.2) are automatically satisfied.] We therefore determine δ_0 and the C_n by the variational condition,

$$\begin{aligned} \delta\int_0^\infty |\Phi_0^{(0)}(r_1=r_2)|^2 dr_1&=0, \quad \text{triplet} \\ \delta\int_0^\infty \left|\frac{\partial}{\partial n}\Phi_0^{(0)}\right|^2_{r_1=r_2} dr_1&=0, \quad \text{singlet.} \end{aligned} \tag{4.7}$$

Substituting (4.4) into the triplet integral in (4.7) gives

$$\begin{aligned} I_T &\equiv \int_0^\infty |\Phi_0^{(0)}(r_1=r_2)|^2 dr_1 \\ &= \int_0^\infty \sin^2(kr+\delta_0)R_{1s}^2(r)dr+2\sum_{j=1}^{N} C_jY_j \\ &\quad + \sum_{j=1}^{N} C_j^2(\mathrm{ME})_{jj}+2\sum_{i>j=1}^{N}\sum C_iC_j(\mathrm{ME})_{ij}, \end{aligned} \tag{4.8}$$

where

$$(\mathrm{ME})_{ij}=\int_0^\infty e^{-(\kappa_i+\kappa_j)r}R_{is}(r)R_{js}(r)dr, \tag{4.9}$$

and

$$\begin{aligned} Y_i&=\int_0^\infty \sin(kr+\delta_0)e^{-\kappa_i r}R_{1s}(r)R_{is}(r)dr \\ &\equiv \mathfrak{N}_{si}\cos\delta_0+\mathfrak{N}_{ci}\sin\delta_0. \end{aligned} \tag{4.10}$$

The variation implicit in (4.7) now becomes

$$\partial I_T/\partial C_i=0, \quad i=1,\cdots,N, \quad \partial I_T/\partial\delta_0=0. \tag{4.11}$$

The first N equations are

$$Y_j+\sum_{i=1}^{N} C_i(\mathrm{ME})_{ji}=0, \quad j=1,\cdots,N,$$

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[14] The presence of the centrifugal terms for $l>0$ is the main reason why the associated Φ_l can be considered separable in zeroth order whereas, $\Phi_0^{(0)}$ cannot.

which may be solved for the C_i to give

$$C_i=\frac{-1}{\det}[D_s^{(i)}\cos\delta_0+D_c^{(i)}\sin\delta_0], \tag{4.12}$$

where det is the determinant of the matrix elements:

$$\det\equiv\det\begin{bmatrix}(\mathrm{ME})_{11} & (\mathrm{ME})_{12} & \cdots & (\mathrm{ME})_{1N}\\ (\mathrm{ME})_{21} & (\mathrm{ME})_{22} & \cdots & (\mathrm{ME})_{2N}\\ \vdots & \vdots & & \vdots\\ (\mathrm{ME})_{N1} & (\mathrm{ME})_{N2} & \cdots & (\mathrm{ME})_{NN}\end{bmatrix}, \tag{4.13}$$

$D_s^{(i)}$ and $D_c^{(i)}$ are determinants gotten by replacing the ith column of the above matrix by the column vectors $(\mathcal{N}_{s1}, \mathcal{N}_{s2}, \cdots, \mathcal{N}_{sn})$ and $(\mathcal{N}_{c1}, \cdots, \mathcal{N}_{cn})$, respectively.

The variation with respect to δ_0 gives

$$\frac{\partial I_T}{\partial\delta_0}=\int_0^\infty \sin[2(kr+\delta_0)]R_{1s}^2dr +2\sum_{i=1}^N C_i\int_0^\infty \cos(kr+\delta_0)R_{is}dr=0. \tag{4.14}$$

Using (4.12) for the C_i, and noting that

$$\sum_{i=1}^N D_s^{(i)}\mathcal{N}_{ci}=\sum_{i=1}^N D_c^{(i)}\mathcal{N}_{si}, \tag{4.15}$$

we can rewrite (4.14) in the form

$$0=\cos(2\delta_0)N_{2s}+\sin(2\delta_0)N_{2c} -\frac{2}{\det}\sin\delta_0\cos\delta_0\sum_{i=1}^N (D_c^{(i)}\mathcal{N}_{ci}-D_s^{(i)}\mathcal{N}_{si}) -\frac{2}{\det}(\cos^2\delta_0-\sin^2\delta_0)\sum_{i=1}^N D_s^{(i)}\mathcal{N}_{ci},$$

where

$$N_{2s}=\int_0^\infty \sin(2kr)R_{1s}^2dr,\qquad N_{2c}=\int_0^\infty \cos(2kr)R_{1s}^2dr. \tag{4.16}$$

We may readily solve for $\tan(2\delta_0)$:

$$\tan(2\delta_0)=-\left[N_{2s}-\frac{2}{\det}\sum_{i=1}^N D_s^{(i)}\mathcal{N}_{ci}\right]\Bigg/\left[N_{2c}+\frac{1}{\det}\sum_{i=1}^N (D_s^{(i)}\mathcal{N}_{si}-D_c^{(i)}\mathcal{N}_{ci})\right]. \tag{4.17}$$

A completely analogous procedure may be used to solve for $\tan2\delta_0$ in the singlet case. One obtains here

$$\tan(2\delta_0)=-\left[\tfrac{1}{2}A_s-kB_c-\frac{2}{\text{dets}}\sum_{i=1}^N \nu_iD_\mu^{(i)}\right]\Bigg/\left[\tfrac{1}{2}A_c+kB_s+\frac{1}{\text{dets}}\sum_{i=1}^N (\mu_iD_\mu^{(i)}-\nu_iD_\nu^{(i)})\right], \tag{4.18}$$

and

$$C_i=(D_\mu^{(i)}\cos\delta_0+D_\nu^{(i)}\sin\delta_0)/\text{dets}. \tag{4.19}$$

Here

$$\text{dets}=\text{determinant}\left\|\int_0^\infty \psi_i\psi_jdr\right\|, \tag{4.20}$$

where

$$\psi_i\equiv\left[\left(-\frac{\partial}{\partial r_1}+\frac{\partial}{\partial r_2}\right)e^{-\kappa_ir_1}R_{is}(r_2)\right]_{r_1=r_2}. \tag{4.21}$$

Let

$$\psi_0\equiv\left[\left(-\frac{\partial}{\partial r_1}+\frac{\partial}{\partial r_2}\right)\sin(kr_1+\delta_0)R_{1s}(r_2)\right]_{r_1=r_2}; \tag{4.22}$$

then μ_i and ν_i are quantities independent of δ_0 defined by

$$-\int_0^\infty \psi_0\psi_idr\equiv\mu_i\cos\delta_0+\nu_i\sin\delta_0.$$

Also

$$A_s\equiv8\int_0^\infty \sin(2kr)[1-2r+(1-k^2)r^2]e^{-2r}dr,$$

$$A_c\equiv8\int_0^\infty \cos(2kr)[1-2r-(1-k^2)r^2]e^{-2r}dr,$$

$$B_s\equiv8\int_0^\infty \sin(2kr)r(1-r)e^{-2r}dr,$$

$$B_c\equiv8\int_0^\infty \cos(2kr)r(1-r)e^{-2r}dr.$$

$D_\mu^{(i)}$ and $D_\nu^{(i)}$ are the determinants gotten by replacing the ith column of dets by the column vectors $(\mu_1,\mu_2,\cdots,\mu_N)$ and $(\nu_1,\nu_2,\cdots,\nu_N)$, respectively.

It is worth pointing out the converse nature of this technique of solution to those usually employed. In most cases one approximates the exact solution in terms of functions which are not solutions of the equation, but do satisfy all the boundary conditions. In close-coupling, for example, the basis functions are solutions of part but not all of the equations. The method that is here presented utilizes functions which are complete solutions of the equation but do not satisfy all the boundary conditions. In the latter method the smallness of the deviation from the boundary condition is a very reliable index of the quality of the solution (providing this difference is small enough).

The method of performing actual calculations is then as follows: A selection of N discrete and/or continuum terms is made (we were necessarily limited to a discrete sampling of the continuum states), and all the matrix elements and integrals in (4.17) and (4.18) evaluated. (Integrals involving discrete states are trivial. Pertinent formulas for continuum states are included in the Appendix.) This, then, can be used to evaluate $\tan2\delta_0$ from (4.17) or (4.18). Knowing $\tan2\delta_0$ determines $(2\delta_0)$ modulo π. The correct quadrant of $(2\delta_0)$ is determined

TABLE I. Triplet results for δ_0.[a]

k				Exchange
0.01	$2, 3, I_0$ 3.11820 -0.165×10^{-7}	$2, 4, I_0$ 3.11823 -0.149×10^{-7}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 3.11821 -0.424×10^{-8}	3.118
0.05	$2, 3, I_0$ 3.0247 0.160×10^{-6}	$2, 4, I_0$ 3.0255 0.168×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 3.0257 0.244×10^{-5}	3.024
0.1	$2, 3, I_0$ 2.9084 0.283×10^{-6}	$2, 4, I_0$ 2.9097 0.465×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 2.9102 0.699×10^{-5}	2.907
0.2	$2, 3, I_0$ 2.6806 0.153×10^{-5}	$2, 4, I_0$ 2.6807 0.173×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 2.6809 0.283×10^{-5}	2.679
0.3	$2, 3, I_0$ 2.4634 0.722×10^{-5}	$2, 4, I_0$ 2.4629 0.433×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 2.4632 0.549×10^{-5}	2.461
0.4	$2, 3, I_0$ 2.2582 0.113×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 2.2588 0.201×10^{-5}	$2, 4, I_0, I_3, I_5, I_7, I_{10}, I_{20}$ 2.2589 0.169×10^{-5}	2.257
0.5	$2, 4, I_0$ 2.0715 0.477×10^{-5}	$2, 4, I_0, I_5, I_{10}, I_{20}$ 2.0716 0.398×10^{-5}	$2, 4, I_0, I_3, I_5, I_7, I_{10}, I_{20}$ 2.0721 0.365×10^{-5}	2.070
0.75	$2, 4, I_0$ 1.6914 0.355×10^{-3}	$2, 3, 4, I_0, I_1, I_2, I_3, I_7$ 1.6830 0.497×10^{-4}	$2, 3, 4, I_0, I_1, I_2, I_3$ 1.6830 0.474×10^{-4}	1.679
0.8	$2, 3, 4, I_0, I_1, I_2, I_3$ 1.61664 -0.117×10^{-4}	$2, 3, 4, I_0, I_1, I_2, I_3, I_7$ 1.61665 -0.123×10^{-4}	$2, 4, I_0, I_3, I_5, I_7, I_{10}, I_{20}$ 1.6220 0.18×10^{-2}	1.614

[a] The first row of each entry refers to the terms used in the expansion of $\Phi_0^{(0)}$. The second row is δ_0 in radians. The third row is the diagonal sum, I_T.

by seeing which value actually minimizes I_T (or I_S). This determines δ_0 modulo π. (At this point it is known for $e-\mathrm{H}$ scattering that $\delta_0\rightarrow\pi$ from below as $k\rightarrow0$, so that in fact no ambiguity remains.[15])

Numerical calculations were coded for the Goddard Division of NASA IBM 7090 computer. The program allowed an arbitrary number of terms (limited only by the capacity of the machine) to be included. In practice, however, we were restricted to less than 10 terms by the following, initially unexpected, circumstance. As we increased the number of terms, both det, dets, and the related determinants approached zero so rapidly that we quickly lost all the significant figures contained in the evaluation of the matrix elements. We therefore had to restrict the number of terms so that at least some significant figures remained. Actually, one does not need to know too many significant figures because one can consider any set of C_i's and δ_0 as an approximate expansion of $\Phi_0^{(0)}$ and measure its quality by the smallness of I_T or I_S.

In Tables I and II we have collected the pertinent results for the triplet and singlet calculations. The last column contains the exchange approximate results which, as was proved earlier, are a variational approximate solution of the zeroth order problem. It is clear that the approximation is in excellent agreement with the exact result.[16] From the tables we see that the triplet phase shifts are less variable and therefore can be more accurately determined than the singlet. This disparity is indicative of the greater accuracy that is obtainable for the triplet results in all parts of the calculation. Note that I_T and I_S are positive definite. These quantities were calculated from (4.8) and its singlet counterpart, using numbers evaluated by the machine from the analytic formulas for $(\mathrm{ME})_{ij}$ etc. The fact that some of the entries are negative is due to the cancellation of all significant figures. Thus, in those

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[15] This example is discussed in connection with an absolute definition of phase shift in A. Temkin, J. Math. Phys. **2**, 336 (1961). The same definition has also been adopted by L. Spruch and L. Rosenberg (reference 3).

[16] Note that N is the number of terms in addition to the first term (which must always be present) in (4.4). In reference 1 we presented results based on using one additional term (the discrete term for $n=2$). The results are almost as good as those of the exchange approximation itself. Since the calculation is a comparatively simple hand calculation, the technique provides an effective way of approximating the much more laborious process of solving the integro-differential equations involved in the exchange approximation. Considerable detail concerning our complete zeroth order calculation will be contained in an article by the author and D. Hoover, in *Methods in Computational Physics*, edited by Alder, Fernbach, and Rotenberg [Academic Press, New York (to be published)], Vol. I.

TABLE II. Singlet results for δ_0.

k					Exchange
0.01	3, 4 3.0638 -0.373×10^{-8}	4, I_0 3.0637 -0.186×10^{-7}	3, I_0, I_3 3.0636 -0.198×10^{-7}	3, 4, I_3, I_4 3.0643 0.242×10^{-7}	3.0606
0.05	4, I_0 2.7595 -0.238×10^{-6}	4, I_0, I_4 2.7596 -0.263×10^{-6}	3, I_0 2.7591 0.157×10^{-6}	3, I_0, I_3 2.7593 0.149×10^{-6}	2.746
0.1	5, I_0, I_5 2.4207 0.774×10^{-6}	4, I_0, I_2, I_3, I_4 2.4174 0.783×10^{-6}	4, I_0, I_3 2.4182 0.918×10^{-6}	4, I_0, I_4, I_8, I_{12}, I_{16} 2.4177 0.934×10^{-6}	2.396
0.2	2, 3, I_1, I_2, I_3, I_4 1.8949 0.777×10^{-5}	2, 5, I_1, I_2, I_3, I_4 1.8968 0.142×10^{-4}	2, I_0, I_1, I_2, I_3, I_4 1.8947 0.193×10^{-4}	3, 4, I_1, I_2, I_3 1.8960 0.253×10^{-4}	1.870
0.3	2, 5, I_1, I_2, I_3, I_4 1.5350 0.183×10^{-4}	2, I_0, I_1, I_2, I_3, I_4, I_5 1.5321 0.291×10^{-4}	2, 4, I_1, I_2, I_3, I_4 1.5348 0.129×10^{-4}	2, 3, I_0, I_6 1.5245 0.295×10^{-4}	1.508
0.4	2, 4, I_1, I_2, I_3 1.2694 0.489×10^{-6}	2, 5, I_1, I_2, I_3, I_4 1.2691 0.150×10^{-5}	2, I_0, I_1, I_2, I_3, I_4 1.2685 0.693×10^{-5}	2, 3, I_2, I_3 1.2697 0.134×10^{-4}	1.239
0.5	3, 4, I_1, I_2 1.0667 0.926×10^{-5}	3, 5, I_1, I_2, I_3, I_4 1.0652 0.353×10^{-4}	2, I_0, I_1, I_2, I_3, I_4, I_5 1.0647 0.375×10^{-4}	2, I_0, I_2, I_4, I_6, I_8 1.0656 0.459×10^{-4}	1.031
0.75	2, 3, 4, $I_{0.75}$, $I_{1.5}$, $I_{2.25}$, I_3, $I_{3.75}$, $I_{4.5}$ 0.7556 0.517×10^{-5}	2, 3, I_0, $I_{0.5}$, I_1, $I_{1.5}$, I_2 0.7564 0.117×10^{-4}	2, 3, 4, $I_{0.5}$, I_1, $I_{1.5}$, I_2, $I_{2.5}$ 0.7535 0.109×10^{-4}	2, I_0, $I_{0.5}$, I_1, $I_{1.5}$, I_2, $I_{2.5}$ 0.7566 0.131×10^{-4}	0.694
0.8	2, 4, 5, $I_{0.75}$, $I_{1.5}$, $I_{2.25}$ 0.7289 0.170×10^{-4}	2, 3, I_0, $I_{0.5}$, I_1, $I_{1.5}$, I_2, $I_{2.5}$ 0.7268 0.175×10^{-4}	2, 3, 4, $I_{0.75}$, $I_{1.5}$, $I_{2.25}$, I_3, $I_{3.75}$, $I_{4.5}$ 0.7261 0.212×10^{-4}	2, 3, 5, $I_{0.5}$, I_1, $I_{1.5}$, I_2, $I_{2.5}$ 0.7273 0.228×10^{-4}	0.651

cases, we have obtained a zero deviation from the boundary condition to within the accuracy of the machine. (The accuracy of the machine is estimated to be from five to seven places.) Because of the loss of significant figures, the smallness of I_T and I_S in Tables I and II cannot be taken as an unambiguous measure of the reliability of δ_0 for the various expansions of $\Phi_0^{(0)}$. Nevertheless, we can obtain somewhat better accuracy in δ_0 than we can currently achieve for the higher order corrections.

The cause for the rapid cancellation of significant figures in the determinants is only a surmise. We think that it is due to the fact that one is trying to approximate solutions of an equation where the solutions are dense. The numerical value of the energy is read into the computer with finite accuracy, and the matrix elements and other integrals are evaluated to about the same but uncorrelated accuracy. The resulting set of equations rapidly becomes one for which many solutions exist. Thus, the determinant of the matrix elements becomes singular, which is what is observed. From a practical point of view this means that one has to retain more significant figures for a final result of a given accuracy than for a bound-state calculation.

V. EVALUATION OF THE MULTIPOLE CORRECTIONS

Granted that the right-hand side of (3.5) converges rapidly, there still remains an assumption which must be fulfilled in order for the effectiveness of this method not to be an illusion. That is that the coupling of the higher Φ_l to the lower Φ_l in (2.4) *not* be such that the omission of the higher Φ_l in the equation for the lower Φ_l make the contribution of the latter to $\sin(\delta-\delta_0)$ substantially different from what it would be if the higher Φ_l were correctly included. Actually, our assumption concerning the importance of the adiabatic contribution implies this situation for small k. For in the adiabatic region only Φ_0 does not vanish, and this coupling is taken into account in (3.6) and (3.7). So, if this region gives the major contribution to the integrals on the right-hand side of (3.5), then we can be sure that the neglect of the higher order couplings cannot materially change the value of the integrals.

We shall introduce a perturbation theory which is based on this assumption. The perturbation theory does not do away with the partial differential equations. (In fact, it is the essence of this method that partial differential equations are the most natural way to include nonadiabaticity both in $\Phi_0^{(0)}$ and the higher Φ_l.) Rather, it allows the equations to be solved in a sequential manner. It also allows the construction of "sum rules" which, to a more limited accuracy, allow for evaluation of the multipole terms without one having to solve the associated partial differential equations beyond what is done in (3.7).[17]

A measure of the adiabaticity of a region of configuration space is the quantity r_2^n/r_1^{n+1}. We shall assign to this quantity an order of magnitude $\lambda^{n/2}$ in accord with the fact that the larger n, the smaller this quantity is in a given region of configuration space. We shall expand the functions Φ_l according to

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

This embodies the notion that the higher Φ_l get successively smaller in the adiabatic region and their behavior away from the adiabatic region can be expanded in a series about their behavior in the adiabatic region.[18] Utilizing these expansions and the order of magnitude associated with adiabatic factor r_2^n/r_1^{n+1}, we can reduce Eq. (2.4) to a set of equations characterized by increasing powers of $\lambda^{\frac{1}{2}}$. To order $\lambda^{\frac{3}{2}}$, we obtain:

$$\lambda^0:\quad (\Delta_{12}+2r_2^{-1}+E)\Phi_0^{(0)}=0. \tag{5.1}$$

$$\begin{aligned}\lambda^{\frac{1}{2}}:\quad &[\Delta_{12}-2(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_1^{(0)}\\ &\qquad=2(3)^{-\frac{1}{2}}r_2r_1^{-2}\Phi_0^{(0)}.\end{aligned} \tag{5.2}$$

$$\lambda:\quad (\Delta_{12}+2r_2^{-1}+E)\Phi_0^{(1)}=2(3)^{-\frac{1}{2}}r_2r_1^{-2}\Phi_1^{(0)}, \tag{5.3}$$

$$\begin{aligned}&[\Delta_{12}-6(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_2^{(0)}\\ &\qquad=2(5)^{-\frac{1}{2}}r_2^2r_1^{-3}\Phi_0^{(0)}.\end{aligned} \tag{5.4}$$

$$\begin{aligned}\lambda^{\frac{3}{2}}:\quad &[\Delta_{12}-2(r_1^{-2}+r_2^{-2})+2r_2^{-1}+E]\Phi_1^{(1)}-\tfrac{4}{5}r_2^2r_1^{-3}\Phi_1^{(0)}\\ &\qquad=2(3)^{-\frac{1}{2}}r_2r_1^{-2}\Phi_0^{(1)}+4(15)^{-\frac{1}{2}}r_2r_1^{-2}\Phi_2^{(0)}.\end{aligned} \tag{5.5}$$

The multipole series (3.5) becomes an expansion in integral powers of λ

$$\begin{aligned}\sin(\delta-\delta_0)=-\frac{1}{k}\sum_{\nu=1}^{\infty}\lambda^{\nu}&\sum_{\substack{m+\mu=\nu\\ m\geq 1,\,\mu\geq 0}}\frac{2}{(2m+1)^{\frac{1}{2}}}\\ &\times\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^m}{r_1^{m+1}}\Phi_m^{(\mu)}dr_1dr_2.\end{aligned} \tag{5.6}$$

λ^{ν} is the expected order of magnitude of the correction to δ_0. The first-order correction is

$$\Delta\delta_0\equiv-\frac{1}{k}\frac{2}{\sqrt{3}}\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2}{r_1^2}\Phi_1^{(0)}dr_1dr_2. \tag{5.7}$$

This is the dipole contribution with the exact Φ_1 replaced by $\Phi_1^{(0)}$. The second-order contribution consists of two terms, $\Delta^2\delta_0^{(1)}+\Delta^2\delta_0^{(2)}$, where

$$\Delta^2\delta_0^{(2)}\equiv\frac{-2}{k\sqrt{5}}\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2^2}{r_1^3}\Phi_2^{(0)}dr_1dr_2, \tag{5.8}$$

$$\Delta^2\delta_0^{(1)}\equiv\frac{-2}{k\sqrt{3}}\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\frac{r_2}{r_1^2}\Phi_1^{(1)}dr_1dr_2. \tag{5.9}$$

$\Delta^2\delta_0^{(2)}$ is of course the perturbation theoretic approximation of the quadrupole term, but $\Delta^2\delta_0^{(1)}$ is a dipole term. It represents the first-order correction on Φ_1 due to the coupling to Φ_0 in the nonadiabatic region. The fact that this term enters in the order λ^2 means that this contribution is expected to be an order of magnitude less than $\Delta\delta_0$. It will be seen that the calculated results are excellently consistent with this assumption.

The calculation itself was carried out to order λ^2. This requires in principle the solution of (5.1) through (5.5). Actually, the fact that one knows the asymptotic form of the functions allows us to achieve reasonably accurate phase shifts without further solving these equations. The adiabatic forms of the functions $\Phi_l^{(0)}$ are:

$$\Phi_l^{(0)}\cong\frac{-2r_1^{-l-1}}{(2l+1)^{\frac{1}{2}}}\sin(kr_1+\delta_0)e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right). \tag{5.10}$$

The asymptotic form of $\Phi_1^{(1)}$ in the adiabatic region is

$$\Phi_1^{(1)}\cong-\frac{2}{\sqrt{3}}(\Delta\delta_0)\frac{\cos(kr_1+\delta_0)}{r_1^2}e^{-r_2}\left(\frac{r_2^3}{2}+r_2^2\right). \tag{5.11}$$

If a large portion of the various integrals comes from the adiabatic region, it is clear that (5.10) and (5.11) alone will give a not unreasonable estimate of their size. One knows more about these functions, namely, their boundary conditions along $r_1=r_2$. In the triplet case the function vanishes, and one can easily append a factor which will do this for $\Phi_l^{(0)}$. We have used

$$\begin{aligned}\Phi_l^{(0)}=\frac{-2\sin(kr_1+\delta_0)}{(2l+1)^{\frac{1}{2}}r_1^{l+1}}&e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_1^{l+1}}{l}\right)\\ &\times(1-e^{-D_l(r_1-r_2)}).\end{aligned} \tag{5.12}$$

D_l is a positive constant which can be fairly unambiguously determined as shown below. In the singlet case there is no truly one-parameter factor which will make the normal derivative of $\Phi_l^{(0)}$ zero along $r_1=r_2$. We have used

$$\Phi_l^{(0)}=\frac{-2}{(2l+1)^{\frac{1}{2}}}\frac{\sin(kr_1+\delta_0)}{(r_1^{l+1}+D_l)}e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right), \tag{5.13}$$

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[17] In conjunction with E. Sullivan and W. Cahill, we have been able to solve the second order partial differential equations numerically. This will be the basis of very precise calculations.

[18] This expansion would not be very good in the region $r_1\cong r_2$ if one were interested in the values of Φ_l. A re-expression of our basic idea is that in order to get good phase shifts, one does not need to know the wave function equally well of all of space. Rather, one must know $\Phi_0^{(0)}$ in all of space (corresponding to the essential 3-body nature of the function) but Φ_l less well, because it is only integrals over these functions which contribute to the phase shift of which the contribution from the configuration space $r_1\cong r_2$ is of only limited importance.

the cutoff factor having been inserted in such a way as to give $\Phi_l^{(0)}$ the expected behavior, $\Phi_l^{(0)} \rightarrow r_1^{l+1}$, in the limit $r_2 \rightarrow r_1 \rightarrow 0$.

The determination of D_l was accomplished in the following way. Using essentially the same method as that used to derive (3.5), one can derive from (5.1) and the equations like (5.2) and (5.4), "sum rules" of the form

$$\int_0^\infty \int_0^{r_1} \Phi_0^{(0)} \left[-l(l+1)\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\right] \Phi_l^{(0)} dr_1 dr_2 = \frac{2}{(2l+1)^{\frac{1}{2}}} \int_0^\infty \int_0^{r_1} \frac{r_2^l}{r_1^{l+1}} (\Phi_0^{(0)})^2 dr_1 dr_2. \quad (5.14)$$

The functions $\Phi_0^{(0)}$ are known from the zeroth order calculation, thus the right-hand sides of (5.14) could be evaluated. The forms (5.12) and (5.13) were used in conjunction with $\Phi_0^{(0)}$ to evaluate the left-hand side as a function of D_l. The adopted values of D_l were those which gave equality. (Some of the results are shown in Figs. 3 and 4.) The adopted values of D_l were then used to evaluate the terms on the rhs of (5.6), in particular $\Delta\delta_0$, $\Delta^2\delta_0^{(2)}$, and $\Delta^2\delta_0^{(1)}$.

The types of cutoff we have used do not introduce any bending of nodal lines in the $r_1 > r_2$ triangle. Such a behavior is reasonable for the lowest energies. At higher energies one expects the bending to become significant, thus the errors intrinsic to the calculation will probably go up.

In calculating $\Delta^2\delta_0^{(1)}$ we have used the same type of cutoff for $\Phi_1^{(1)}$ as for $\Phi_1^{(0)}$. One can derive "sum rules" which tend to indicate that the value of D to be used should be somewhere between the dipole value D_1 and the quadrupole D_2. Nevertheless the contribution of this function from the nonadiabatic region is expected to be greater relative to its contribution from the adiabatic region. In addition, judging from (5.5), its behavior in the nonadiabatic region is expected to be much more complicated there. Thus, our evaluation of $\Delta^2\delta_0^{(1)}$ should be considered somewhere between a calculation and an estimate.

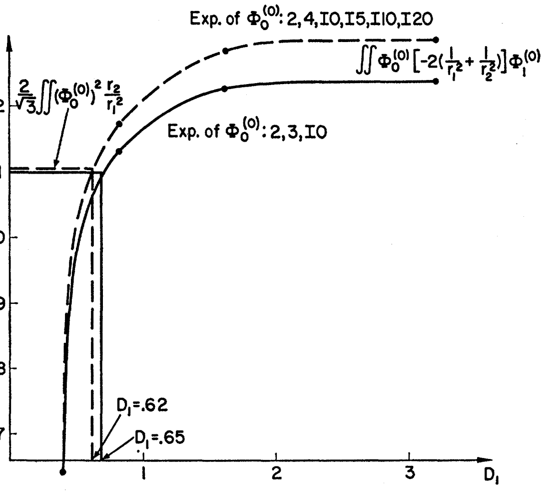

FIG. 3. Triplet dipole sum rule for $k=0.1$ and two different expansions of $\Phi_0^{(0)}$. The values of $\Delta\delta_0$, using the two expansions of $\Phi_0^{(0)}$ and the respective values of D_1 in $\Phi_1^{(0)}$, are 0.0303 and 0.0304.

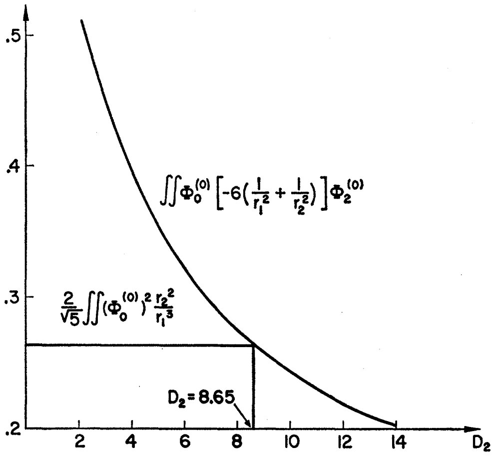

FIG. 4. Singlet quadrupole sum rule for $k=0.5$. Different expansions of $\Phi_0^{(0)}$ give curves which are indistinguishable on this scale. The value of $\Delta^2\delta_0^{(2)}$ for this case is 0.0232.

In practice, all double integrals were done numerically. We were thus forced to stop the integration over r_1 at a finite point $r_1 = R$. It is important, however, to take into account the contribution of the integral for $r_1 > R$ in the limit of zero energy. This fortunately can be done analytically. The analysis for the effect of this long-range behavior on the scattering length has already been given.[19] A somewhat more general derivation yields

$$a = a(R) - \alpha\left(\frac{1}{R} - \frac{a+a_0}{2R^2} + \cdots\right), \quad (5.15)$$

where $\alpha = \frac{9}{2}$ is the polarizability of atomic hydrogen, a is the exact scattering length, and a_0 is the scattering length of the zeroth order problem. $a(R)$ is the scattering length associated with the part of the wave function within radial distances of R of the nucleus. Formula (5.15) is another result of long-range induced polarization indicative of the basic difference between a bound state and a scattering problem. For a value of $R = 25$, a bound-state wave function has essentially assumed its asymptotic form, whereas the portion of the wave function beyond $R = 25$ contributes (negatively) almost 10% to the triplet scattering length.[19] Equation (5.15) is valid for any method in which only the part of the configuration space for r_1, $r_2 < R$ is included.

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[19] This analysis is contained in A. Temkin, Phys. Rev. Letters **6**, 354 (1961), together with the result of our triplet scattering length calculation. At that time the significant reduction from the RSO bound (reference 2) was completely unexpected. We were subsequently informed that the α/R term has been derived on the basis of the Born approximation by R. M. Thaler, Phys. Rev. **114**, 827 (1959).

TABLE III. Resume of calculation for triplet δ.

k	δ_0	$\Delta\delta_0$	$\Delta^2\delta_0^{(1)}$	$\Delta^2\delta_0^{(2)}$	δ	δ (pol. orb.)
0[a]	2.338(3)				1.76(3)	1.7[b](1)
0.01	3.11821(2)	0.00504	0.000295	0.000153	3.1237(4)	3.125[b]
0.05	3.025(1)	0.0193	0.0013	0.0008	3.046(5)	3.049[b]
0.1	2.909(1)	0.0303	0.0021	0.0014	2.942(10)	2.946[b]
0.2	2.6810(5)	0.0379	0.0021	0.0023	2.723(10)	2.732
0.3	2.4630(5)	0.0392	0.0017	0.0026	2.516(10)	2.519
0.4	2.259(1)	0.0379	0.0013	0.0028	2.301(10)	2.320
0.5	2.072(1)	0.0363	0.0011	0.0027	2.112(10)	2.133
0.75	1.683(2)	0.0328	0.0007	0.0024	1.719(10)	1.745
0.8	1.617(2)	0.0282	0.0005	0.0018	1.647(10)	

[a] The $k=0$ entries are scattering lengths.

[b] These pol. orb. results are slightly different from those given in Temkin-Lamkin (reference 20) due to the fact that integration there was stopped at $r=20$.

The contributions from large r die off rapidly as k is increased to the extent that they are negligible for our accuracy by $k=0.1$. Tables III and IV contain a summary of the singlet and triplet calculated results. The δ_0 are a somewhat visual mean of the values in Tables I and II. The convergence of the higher terms is evident. The final δ contain in parentheses the estimated accuracy of the last figure(s). The convergence is such that all higher multipole contributions should be smaller than this error. The error is again an estimate of those due to δ_0 and the higher multipoles. (The quantities in parentheses in the other columns are not deviations from the electron-hydrogen phase shifts, but rather from the exact phase shifts of well-defined but different mathematical problems.) The greatest absolute error of the higher multipoles is contained in $\Delta\delta_0$ (although it contains the smallest proportional error.) In the triplet case we have estimated the error from about 5% to 25% for increasing k. In the singlet case, the estimated error ranged from 10% to 40%. We feel that the errors we have allowed for are rather liberal, particularly in the triplet case. For that reason, we have retained more figures than would seem to be justified by the error. In the last column we have included the polarized orbital phase shifts.[20]

VI. DISCUSSION

The implications of the nonadiabatic theory for the various well-known techniques of calculating (s-wave) scattering problems are clear. The exchange approximation as representative of the zeroth order problem has a central role and is by no means a bad approximation. The method of polarized orbitals[20] and to a lesser extent the various exchange adiabatic approximations[21,22] are legitimate next order correction. The application of these conclusions for electron scattering from other atoms is perhaps even more significant. For in those cases one cannot readily do better than the exchange approximation. But since one expects the polarization to act even more classically, the inclusion of an exchange-adiabatic polarization potential would seem eminently worthwhile, where the atomic polarizability is non-negligible. The quantitative alteration, in fact, can be much more pronounced than in hydrogen. In oxygen, for example, the polarization potential decreases the zero-energy exchange approximate cross section by a factor of 8, and by a factor of 2 at energies of 10 ev.[21,23] Both decreases seem now to be confirmed by experiment.[24]

There are, however, at least two related problems which it would also be well to put on a rigorous basis at least in the case of hydrogen. One is the scattering of higher than s partial waves, the second is the inelastic scattering.

Concerning the first problem, one feels that physical intuition should be a reasonable guide as to what techniques are best. Thus, for a given incident energy one would expect the phase shifts to get increasingly further from the exchange approximation phase shifts. This is expected to be so because the higher partial waves are concentrated further from the center, where the adiabatic potential becomes increasingly important relative to other effects. Or, to put it another way, for a given incident velocity, the further away a particle orbit, the more adiabatic its motion appears (an observation we have all verified on passing airplanes).[25] Nevertheless, the solution of this problem by an extension of our nonadiabatic theory is not trivial. This is because the Schrödinger equation reduces to sets of three-dimensional coupled partial differential equations.[9] In addition, at the lowest energies the polarization must be included in the zeroth order approximation corre-

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[20] A. Temkin and J. Lamkin, Phys. Rev. **121**, 788 (1961).

[21] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

[22] B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958).

[23] A. Temkin, Phys. Rev. **107**, 1004 (1957).

[24] S. C. Lin and B. Kivel, Phys. Rev. **114**, 1076 (1959). R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. **123**, 148 (1961).

[25] The picture may not be as rosy as one thinks. Recent experiments by R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo [Phys. Rev. **124**, 135 (1961)] of the $e-H$ total elastic cross section, if they are correct, would indicate that the triplet p-wave phase shifts are much closer to the exchange approximate results. This heightens the necessity for a rigorous quantitative theory for the higher partial waves.

TABLE IV. Resume of calculation for singlet δ.

k	δ_0	$\Delta\delta_0$	$\Delta^2\delta_0^{(1)}$	$\Delta^2\delta_0^{(2)}$	δ	δ (pol. orb.)
0	7.8(1)				5.6(4)	5.7
0.01	3.0640(5)	0.026	−0.008	0.004	3.086(4)	3.085(1)
0.05	2.759(1)	0.117	−0.035	0.019	2.86(2)	2.86
0.1	2.420(3)	0.187	−0.045	0.030	2.59(3)	2.58
0.2	1.895(2)	0.215	−0.030	0.034	2.11(5)	2.11
0.3	1.535(10)	0.189	−0.016	0.030	1.74(6)	1.75
0.4	1.269(1)	0.165	−0.009	0.026	1.45(6)	1.47
0.5	1.066(2)	0.148	−0.007	0.023	1.23(6)	1.25
0.75	0.756(2)	0.131	−0.0025	0.021	0.91(6)	0.91
0.8	0.728(2)	0.126	−0.002	0.020	0.87(6)	

sponding to the fact that the effective-range formula gets altered in its first term.[22,26]

The second problem is also difficult to handle by our present method. Consider for example the s-wave part of the $1s-2s$ excitation problem. This is a zero orbital angular momentum equation governed again by (2.1). The difficulty here is in the boundary condition (2.8) must contain all states that are energetically accessible. Even the solution of the zeroth equation (3.3) is enormously complicated for the same reason. One is restricted to the statement that present s-wave close-coupling approximations which include only s-excited states of hydrogen[27] are again approximations of only the zeroth order problem (3.3). Here, however, it appears that the zeroth order problem is a much more uncertain approximation of the whole problem.

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APPENDIX

We give here formulas for integrals involving continuum Coulomb wave functions. We would like to acknowledge the guidance of Dr. L. Maximon in performing these integrations. All formulas are obtainable from the very general formulas of Alder *et al.*[28] The results involve, among others, the various kinds of hypergeometric and Bessel functions. The notation for these are standard aside from minor variations. Definitions may be found in innumerable books; we mention only Morse and Feshbach.[9] Many of the formulas are not manifestly real; nevertheless, they may all be shown to be real. Those matrix elements which should be symmetric with respect to the interchange of initial and final states can be shown to be symmetric. The reality and symmetry are, in fact, closely related.

The continuum Coulomb functions are normalized as follows:

$$u_p(r)=re^{-ipr}F(1+i/p;2;2ipr),$$
$$u_0(r)=\lim_{p\to 0}u_p(r)=(r/2)^{\frac{1}{2}}J_1((8r)^{\frac{1}{2}}).$$

$F(a;b;x)$ is the confluent hypergeometric function; $J_n(x)$ is the Bessel function of order n. In practice, all integrals involving the zero-energy Coulomb wave function $u_0(r)$ (denoted by the index $I0$) can be derived from the formulas involving a general p (denoted by Ip) by suitable limiting processes. For the purpose of giving the discrete-continuum matrix elements it is convenient to write the discrete wave functions in the form

$$R_{ns}(r)=e^{-r/n}\sum_{j=1}^{n}C_{nj}r^j,$$

where C_{nj} is the coefficient of r^j in

$$R_{ns}(r)=(n)^{-\frac{1}{2}}(2rn^{-1})e^{-(r/n)}F(-n+1;2;2rn^{-1}).$$

All $\tan^{-1}$ functions are to be taken between $-\pi/2$ and $\pi/2$. Triplet formulas:

$$(\mathrm{ME})_{Ip1,Ip2}=\left\{\left[2\lambda\exp\left(\frac{p_1-p_2}{p_1p_2}\tan^{-1}\frac{(p_1-p_2)}{\lambda}-\frac{p_1+p_2}{p_1p_2}\tan^{-1}\frac{(p_1+p_2)}{\lambda}\right.\right.\right.$$
$$\left.\left.\left.+i\frac{(p_2-p_1)}{2p_1p_2}\ln\left(\frac{\lambda^2+(p_1-p_2)^2}{\lambda^2+(p_1+p_2)^2}\right)\right)\right]\Big/[\lambda^2+(p_1-p_2)^2][\lambda^2+(p_1+p_2)^2]\right\}$$
$$\times\left\{F(-ip_2^{-1},ip_1^{-1};1;x)-\frac{2y[\lambda+i(p_1-p_2)]}{\lambda^2+(p_1-p_2)^2}F(1-ip_2^{-1},1+ip_1^{-1};2;x)\right\},$$

where $F(a,b;c;x)$ are hypergeometric functions, $\lambda=\kappa_{p1}+\kappa_{p2}$, $x=4p_1p_2/[\lambda^2+(p_1+p_2)^2]$, and $y=1-x$.

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[26] R. Thaler, Phys. Rev. **114**, 827 (1959). L. Spruch, T. O'Malley, and L. Rosenberg, Phys. Rev. Letters **5**, 375 (1960).

[27] K. Smith (reference 12). R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).

[28] K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther, Revs. Modern Phys. **28**, 432 (1956). See in particular formula (II. B. 53).

$$(\mathrm{ME})_{I0,Ip}=\frac{2\lambda}{(\lambda^2+p^2)^2}\exp\left(\frac{-2\lambda}{\lambda^2+p^2}-\frac{2}{p}\tan^{-1}\frac{p}{\lambda}+\frac{2ip}{\lambda^2+p^2}\right)\left[F\left(ip^{-1};1;\frac{-4ip}{\lambda^2+p^2}\right)-\frac{2(\lambda+ip)}{\lambda^2+p^2}F\left(1+ip^{-1};2;\frac{-4ip}{\lambda^2+p^2}\right)\right],$$

where $\lambda=\kappa_0+\kappa_p$.

$$(\mathrm{ME})_{I0,I0}=2\lambda^{-3}e^{-4/\lambda}\{I_0(4\lambda^{-1})-I_1(4\lambda^{-1})\},$$

where $\lambda=2\kappa_0$ and $I_m(x)$ are the Bessel function of imaginary argument.

$$(\mathrm{ME})_{n,Ip}=\sum_{j=1}^{n}C_{nj}\mathcal{G}_j(\lambda_{np}).$$

where $\lambda_{np}=\kappa_n+\kappa_p+n^{-1}$, $\mathcal{G}_j(\lambda)=\int_0^\infty e^{-\lambda r}r^ju_p(r)dr$, hence $\mathcal{G}_j(\lambda)=-(\partial/\partial\lambda)\mathcal{G}_{j-1}(\lambda)$, and

$$\mathcal{G}_0(\lambda)=(\lambda^2+p^2)^{-1}\exp[-2p^{-1}\tan^{-1}(p/\lambda)].$$

$$(\mathrm{ME})_{n,I0}=\lim_{p\to0}(\mathrm{ME})_{n,Ip}.$$

$$\mathcal{N}_{s,Ip}=2S(\lambda_p)\sin\theta,\quad \mathcal{N}_{c,Ip}=2S(\lambda_p)\cos\theta,$$

$$\lambda_p=1+\kappa_p,$$

$$S(\lambda_p)=[2\lambda_p^2(1+p^2)^{\frac{1}{2}}]^{-1}\exp(-p^{-1}\tan^{-1}p),$$

$$\theta=\tan^{-1}(k/\kappa_p)+\frac{1}{2p}\ln\left[\frac{\lambda_p+p(p-k)}{\lambda_p+p(p+k)}\right].$$

$$\mathcal{N}_{s,I0}=\lim_{p\to0}\mathcal{N}_{s,Ip},\quad \mathcal{N}_{c,I0}=\lim_{p\to0}\mathcal{N}_{c,I0},$$

where the only nontrival limit is

$$\theta_0=\tan^{-1}(k/\kappa_0)-k\lambda_0^{-1}.$$

Singlet formulas (the symbols have the same meaning as the corresponding triplet formulas):

$$(\mathrm{SME})_{Ip1,Ip2}=[2\kappa_{p1}\kappa_{p2}+p_2^2+\kappa_{p2}^2+\lambda^{-1}\kappa_{p1}(\lambda^2+p_1-p_2^2)](\mathrm{ME})_{Ip1,Ip2}$$
$$+2\exp\left[\frac{p_1-p_2}{p_1p_2}\tan^{-1}\left(\frac{p_1-p_2}{\lambda}\right)-\frac{p_1+p_2}{p_1p_2}\tan^{-1}\left(\frac{p_1+p_2}{\lambda}\right)+\frac{i(p_2-p_1)}{2p_1p_2}\ln y\right]\frac{F(1-ip_2^{-1},1+ip_1^{-1};2;x)}{\lambda^2+(p_1+p_2)^2},$$

$$(\mathrm{SME})_{Ip,I0}=[2\kappa_p\kappa_0+\kappa_0^2+\lambda^{-1}\kappa_p(\lambda^2+p^2)](\mathrm{ME})_{Ip,I0}$$
$$+2\exp\left[\frac{2\lambda}{\lambda^2+p^2}+\frac{2}{p}\tan^{-1}(p/\lambda)+\frac{2ip}{\lambda^2+p^2}\right](\lambda^2+p^2)^{-1}F\left(1+ip^{-1};2;\frac{-4ip}{\lambda^2+p^2}\right),$$

$$(\mathrm{SME})_{I0,I0}=\frac{e^{-4/\lambda}}{2\lambda}\left\{5I_0\left(\frac{4}{\lambda}\right)-3I_1\left(\frac{4}{\lambda}\right)\right\},$$

$$(\mathrm{SME})_{n,Ip}=(\kappa_n-n^{-1})\sum^{n}C_{nj}\{(\kappa_n+\lambda_{np})\mathcal{G}_j(\lambda_{np})-j\mathcal{G}_{j-1}(\lambda_{np})\}+\sum_{j=1}^{n}C_{nj}j\{(\kappa_n+\lambda_{np})\mathcal{G}_{j-1}(\lambda_{np})-(j-1)\mathcal{G}_{j-2}(\lambda_{np})\},$$

$$(\mathrm{SME})_{n,I0}=\lim_{p\to0}(\mathrm{SME})_{n,Ip},\qquad \mu_{Ip}=N_{srIp}-N_{sIp}+kN_{crIp},\qquad \nu_{Ip}=N_{crIp}-N_{cIp}-kN_{srIp},$$

where

$$N_{srIp}=2S(\lambda_p)[\kappa_n\sin\theta-k\cos\theta],$$

$$N_{sIp}=2(\kappa_n+1)S(\lambda_p)[(2\kappa_n+1)\sin\theta-k\cos\theta],$$

$$N_{crIp}=2S(\lambda_p)[\kappa_n\cos\theta+k\sin\theta],$$

$$N_{cIp}=2S(\lambda_p)(1+\kappa_n)[(2\kappa_n+1)\cos\theta+k\sin\theta],$$

$$\mu_{I0}=\lim_{p\to0}\mu_{Ip},$$

$$\nu_{I0}=\lim_{p\to0}\nu_{Ip}.$$