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Absolute Definition of Phase Shift in the Elastic Scattering of a Particle from Compound Systems

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The projection of the target wave function on the total wave function of a scattered particle interacting with the target system is used to define an absolute phase shift including any multiples of π. With this definition of the absolute phase shift, one can prove rigorously in the limit of zero energy for s-wave electrons scattered from atomic hydrogen that the triplet phase shift must approach a nonzero multiple of π. One can further show that at least one π of this phase shift is not connected with the existence of a bound state of the H^- ion.

I. INTRODUCTION

IN the scattering of a particle from a local central potential, Levinson[1] has proved an interesting and important theorem; as it applies to attractive potentials, it says that the number of nodes in the zero-energy radial wave function is equal to the number of bound states which the potential will allow. (For the purposes of this discussion, we confine ourselves to s-wave scattering.) The zero-energy phase shift δ is related to the number of nodes by

$$\delta = n\pi, \quad n=0, 1, 2, \cdots. \tag{1.1}$$

(For an attractive potential, we use the usual convention of choosing the phase shift as positive.)

It should be noted that in this one-body problem the phase shift at any energy has an absolute significance. It is the absolute phase difference between the radial wave function and the spherical Bessel function measured from the origin to where the phase difference becomes constant. This phase difference is the absolute phase shift. It is sufficient for our purposes to define the absolute phase of a function (in radians) at a point as the ratio of the length from the previous node to the abscissa of the point divided by the length between the surrounding nodes, plus the number of nodes up to and including the previous node (but excluding the origin) all times π. (See Fig. 1.)

There has been some interest in extending Levinson's theorem to the case of a particle scattered from targets consisting of more than one particle. In these cases, however, there is as far as we know no universally accepted definition of an absolute phase shift. Clearly, such a definition is a necessary step in extending Levinson's theorem to the compound target case. An obvious approach to such a definition is to associate a one-particle radial wave function with the many-body scattering process; then one can use the above procedure to determine its absolute phase. We shall argue that

$$u_k(r_0) \equiv r_0 \int \Phi_0^*(1,2,\cdots,N)\Psi_k(0;1,2,\cdots,N)dr_0^{-1} \tag{1.2}$$

[1] Norman Levinson, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd 25, No. 9 (1949). The reason these theorems are restricted to zero impacting energy is because for nonzero energy the scattered wave function is always sinusoidal at infinity and, therefore, contains an infinite number of nodes. In the zero-energy case, the scattered wave function degenerates into a straight line, and the number of nodes becomes finite. There are various conditions which the potential must have in order for Levinson's proof to be valid. The most important is that it cannot have more than a Coulomblike singularity at the origin.

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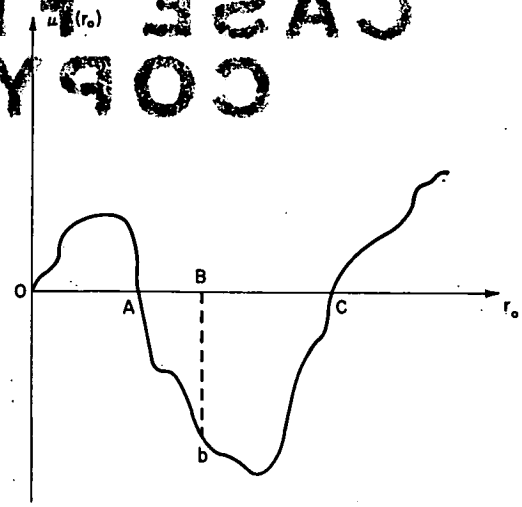

FIG. 1. Absolute phase of a function $u_k(r_0)$. In the diagram, phase of u_k at b is $(1+\langle AB\rangle/\langle AC\rangle)\pi$. Note that bumps in the function $u_k(r_0)$ do not contribute integral multiples of π to phase unless they cause u_k to cross the axis.

provides a consistent definition of such an equivalent one-particle radial wave function.[2] (u_k should always be understood as r_0 times the radial wave function. dr_0^{-1} signifies integration over all coordinates but r_0.) Indeed, the above expression, which is the projection on the target wave function Φ_0 of the exact wave function of the target system plus incoming particle Ψ_k, has tacitly been assumed by some people. However, alternate means of defining the phase shift have been used. For instance, in the scattering of neutrons from nuclei, it is customary to compute the phase shift from formulas relating it to the logarithmic derivative at a point where the interaction is assumed to be negligible. In so doing, one has renounced altogether defining a phase shift except modulo π. There is some justification in this approach on the ground that when the incoming particle is interacting strongly with the target system, the wave function is highly nonseparable; then the idea of a phase shift loses all meaning. However, no matter how complicated the wave function, it is clear that (1.2) does tell how much on the average the incoming particle is being attracted or repelled by the target. What we are really asking is whether this definition of the phase shift, which traces the buildup of the phase shift as a function of r_0, will not alter (correctly) calculated results.

However, that the definition (1.2) cannot change results modulo π is abundantly clear. For in order that a phase shift be defined in a given process, Ψ_k must have the asymptotic form

$$\lim_{r_0\to\infty}\Psi_k=\sin(kr_0+\delta')\Phi_0+\sum_{j\neq 0}h_j(r_0)\Phi_j(1,\cdots,N),$$

where the Φ_j for $j\neq 0$ refer to other states (including perhaps dissociated states) of the target system (for which the h_j do not vanish). All these states have in common that they are orthogonal to the original state of the target. Thus, substituting the above into (1.2), we see that

$$\delta=\delta'+l\pi.$$

In Sec. II we shall discuss the Hartree-Fock approximation for scattering, in particular Swan's[3] conjecture of the extension of Levinson's theorem, which is intimately connected with it. A different method of determining phase shifts is also analyzed in that section. Section III contains a rigorous yet trival demonstration that the triplet, zero-energy phase shift in the scattering of electrons from atomic hydrogen is a nonzero multiple of π. One can show that this behavior need have nothing to do with the existence of triplet bound state of the composite system which is the H^- ion.

II. ALTERNATE METHODS OF DETERMINING THE MANY-PARTICLE PHASE SHIFT AND SWAN'S CONJECTURE

A particularly important case of scattering from a compound target is the scattering of electrons from atoms. One of the most established methods of treating this problem is the exchange or Hartree-Fock approximation.[4] According to this approximation, one makes an Ansatz for the total wave function of an antisymmetrized product of an undetermined function $\tilde{u}_k(r_0)$ of the scattered particle times the ground state wave function of the atom Φ_0:

$$r_0\Psi_k=\mathcal{A}\{\tilde{u}_k(r_0)\Phi_0(1,2,\cdots,N)\}. \tag{2.1}$$

$\mathcal{A}$ is the antisymmetrizer; Φ_0 is considered already antisymmetrized. The variational principle (H is the Hamiltonian of the total system and E the total energy),

$$\delta\int\Psi_k^*(H-E)\Psi_k d\tau=0, \tag{2.2}$$

is used to derive a one-dimensional integro-differential equation for $\tilde{u}_k$, from which the phase shift is determined precisely as in the one-body problem. Here then, one has a prescription for calculating an absolutely defined phase shift, which, however, has the disadvantage of being tied to an approximate Ansatz for the wave function. Within this approximation, Swan[4] has conjunctured an extension of Levinson's theorem which says, concerning the zero-energy phase shift δ,

$$\delta=(n+m)\pi, \tag{2.3}$$

[2] We assume that Ψ_k is real. We have always found that one can so choose Ψ_k providing one is dealing with a given partial wave (such that Ψ_k is a state of good total angular momentum) below the threshold for any inelastic process.

[3] P. Swan, Proc. Roy. Soc. (London) A228, 10 (1955). This important paper is unfortunately not clear. In particular, the conjecture is put in the form of a theorem, but it is not clear to what extent his subsequent arguments are intended to be a proof of the theorem.

[4] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933). See also E. Feenberg, Phys. Rev. 40, 40 (1932); 42, 17 (1932).

where n is, as above, the number of composite bound states that the potential will allow, and m is the number of states from which the particle is excluded by the Pauli principle. An example of the meaning of m is the following. Consider the s-wave scattering of a particle from an atom whose (Hartree-Fock) wave function has filled $1s$ and $2s$ shells. Both these shells are excluded so that the zero-energy wave function would be expected to have at least two nodes according to Swan's theorem. If, in addition, the negative ion would have a bound state in which the additional particle were in a $3s$ state, then an additional node would be induced in the zero-energy scattered wave function.

We wish to investigate the connection of the function $\tilde{u}_k$ with u_k of (1.2), assuming we replace the exact Ψ_k by the exchange approximate (2.1).

From the considerations of Sec. I we know that $\tilde{u}_k$ and u_k will give rise to the same phase shift modulo π. What we want to know is how these functions compare for smaller values of r_0. Because of the antisymmetry of (2.1), one can add to $\tilde{u}_k$ any amount of any orbitals which have the same angular and spin dependence (assumed to be s orbitals in the case of s-wave scattering) without changing Ψ_k. For instance, in the example discussed above, one can add any amount of $1s$ or $2s$ to $\tilde{u}_k$ without affecting Ψ_k, and in general a $\tilde{u}_k = \tilde{U}_k$ can always be found which is orthogonal to all the orbitals of the Hartree-Fock wave function. *The virtue of (1.2) as it applies to the Hartree-Fock approximation is that it automatically generates such a* $\tilde{U}_k$. It is to such a $\tilde{U}_k$ that Swan's theorem is meant to apply.[5] From the theory of linear second-order equations (in particular the radial hydrogen equations), one would expect the scattered "orbital" in the example to have at least one more node that u_{2s}, which would mean that it would have at least two nodes. [See example connected with Eq. (3.5a).] The existence of bound states would then, in the usual way, induce additional nodes, and this is the heuristic basis of Swan's conjecture. (The argument is not rigorous because $\tilde{u}_k$ does not satisfy an ordinary differential equation, but rather an integro-differential equation.) The only part of Swan's assertion which can be rigorously salvaged from the theorem of Sec. III is that the zero-energy s-wave phase shift of an electron scattered from an atom with a filled $1s$ shell must approach at least π.

There arises here as in the one-body problem an ambiguity in the over-all sign of the phase shift. In the one-body problem, this ambiguity is settled, where the radial function $u_k(r)$ is known, by choosing that sign for $u_k(r)$ such that $u_k'(0)>0$. In our case, this means choosing that sign for Ψ_k such that the same condition for $u_k(r_0)$ applies.[6] In both cases, the phase shift is the difference between the phase of $u_k(r_0)$ and that of $+\sin kr_0$. This assures that an attractive potential produces a positive phase shift.

It may be thought at this point that we are getting very much out of this procedure for determining the absolute phase shift. However, one should bear in mind that we are using considerably more information contained in the total wave function than its asymptotic form. In particular, by using the projection of the total wave function on the ground state, we are including some aspects of its behavior right down to the origin.

In some applications, the phase shift has been determined by the condition that it approach zero as the energy becomes infinite, and that it vary continuously as the energy varies. We should like to point out that the first condition is not necessarily true and that the second can be misleading. An obvious counter example of the first condition is a system with hard-core potentials. Here, the region in which the wave function differs from its asymptotic form does not vanish as the energy is increased indefinitely, and the phase shift does not approach zero. Concerning the second condition, it must be emphasized that although the phase shift is a continuous function of the energy, its slope need not be continuous and will in fact be discontinuous whenever the threshold for some competing process is reached. Since in any numerical calculation one can only find phase shifts for some finite set of k's, it is possible that a discontinuity in slope of δ as a function of k may appear as a discontinuity in δ itself. In some variational calculations where the variational expression may have several relative minima as a function of k, such a behavior might cause the wrong branch to be followed.

III. PROOF THAT THE ZERO-ENERGY TRIPLET PHASE SHIFT IN THE SCATTERING OF ELECTRONS FROM HYDROGEN IS A NONZERO MULTIPLE OF π

Let $\Psi_-(\mathbf{r}_0,\mathbf{r}_1)$ be the exact wave function of the zero-energy triplet $e-$H system. Then,

$$\Psi_-(\mathbf{r}_0,\mathbf{r}_1) = -\Psi_-(\mathbf{r}_1,\mathbf{r}_0). \tag{3.1}$$

Now expand

$$\Psi_-(\mathbf{r}_0,\mathbf{r}_1) = \sum_n \psi_n(\mathbf{r}_0)\varphi_n(\mathbf{r}_1), \tag{3.2}$$

where φ_n are the states of the hydrogen atom. According to our definition, the absolute phase shift is determined from

$$\psi_0(\mathbf{r}_0) = \int \varphi_0^*(\mathbf{r}_1)\Psi_-(\mathbf{r}_0,\mathbf{r}_1)d\mathbf{r}_1. \tag{3.3}$$

[5] The Hartree-Fock orbitals of nonclosed shell atoms are not in general orthogonal. Nevertheless one can always orthonormalize them without changing the Slater determinant. We shall always think of the determinantal Hartree-Fock wave function whose orbitals are orthonormalized. The fact that $\tilde{u}_k$ could be made orthogonal to the Hartree-Fock orbitals was realized by Feenberg (footnote 4).

[6] This prescription only applies where the wave function is defined over all space. It therefore is not suitable without modification for such things as hard-core potentials. Assuming the potential to be allowable, the prescription implies that a repulsive potential can only give rise to a phase shift of 0 as $k \to 0$; i.e., it cannot be any other negative multiple of π. In the one-body case, this is implicit in Levinson's theorem (footnote 1).

Now use (3.1) and (3.2) on the rhs of (3.3), and multiply both sides by $\varphi_0^*(r_0)$ and integrate over $\mathbf{r}_0$ to get

$$\int \varphi_0^*(\mathbf{r}_0)\psi_0(\mathbf{r}_0)d\mathbf{r}_0 = -\int \varphi_0^*(\mathbf{r}_1)\psi_0(\mathbf{r}_1)d\mathbf{r}_1. \quad (3.4)$$

From this, we conclude finally

$$\int_0^\infty u_0(r_0)u_{1s}(r_0)dr_0 = 0, \quad (3.5)$$

where

$$\psi_0(\mathbf{r}_0) = [u_0(r_0)/r_0]Y_{00}(\Omega_0),$$

and

$$\varphi_0(\mathbf{r}_0) = [u_{1s}(r_0)/r_0]Y_{00}(\Omega_0) \equiv \varphi_{10}(\mathbf{r}_0).$$

This proof is implicit in the work of Mittleman,[7] in which he constructs an equivalent (nonlocal) potential for $\psi_0(\mathbf{r}_0)$ for which the orthogonality property is preserved at every stage of approximation. However, by virtue of our definition of absolute phase shift, we can readily go one step further and say that this implies the triplet phase is a nonzero multiple of π. For the function $u_{1s} = 2r_0e^{-r_0}$ has no nodes; therefore, the function $u_0(r_0)$ must have at least one node. From our method of computing phase shifts, it follows that this is equivalent to the phase shift being $n\pi$ where $n>0$ is the number of nodes in $u_0(r_0)$ (neglecting the measure zero probability that the slope of u_0 is horizontal at $r_0=\infty$, which would add another $\pi/2$ onto the phase shift[1]). To show that at least one of these nodes is not connected with the existence of a triplet bound state of the H^- ion, one need only consider the case where the repulsion between the electrons was increased and the attraction of the electrons to the nucleus was decreased. It is clear that a point would be reached for it to be physically inconceivable for a bound state to exist. Yet everything in the above proof would go through, and there would still have to be at least one node in $u_0(r_0)$.

It is worth noting in the proof of orthogonality that the eigenfunction character of $\Psi_-(\mathbf{r}_0,\mathbf{r}_1)$ with respect to the total Hamiltonian is not used. This has as a consequence the fact that if one uses any antisymmetric Ansatz for Ψ_- and computes an equivalent one-particle orbital and phase shift as defined above, then the nodal behavior of this function and the orthogonality still apply. As a trivial example, consider the Ansatz

$$\Psi_-(r_0,r_1) = (4\pi)^{-\frac{1}{2}}\left\{\frac{\sin kr_0}{r_0}\varphi_{10}(r_1) - \frac{\sin kr_1}{r_1}\varphi_{10}(r_0)\right\}. \quad (3.5a)$$

If we compute $u_k(r_0)$ according to (1.2), confining ourselves to the $k=0$ case, we find

$$\lim_{k\to 0} u_k(r_0)/k = r_0(1-8e^{-r_0}).$$

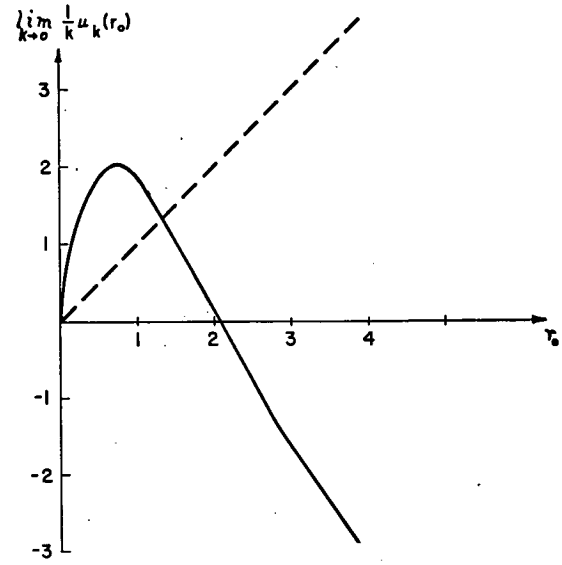

FIG. 2. Solid curve is plot of $k^{-1}u_k(r_0) = k^{-1}r_0\int \varphi_{10}\Psi_- dr_1$, where Ψ_- is given in Eq. (3.5a) for $k=0$. The phase shift in this case is π. Dashed line is scattered function before orthogonalization to ground state function. For that curve phase shift is zero.

A simple integration shows that this function is orthogonal to $u_{1s}(r_0)$, and it is also clear that the function has one node at $r_0 = \ln 8$. [Note that $8r_0e^{-r_0}$ is a multiple of $u_{1s}(r_0)$.] If we had concentrated our attention on $k^{-1}\sin kr_0 \to r_0$ as $k\to 0$, then we would have said the phase shift approached 0 (see Fig. 2). The function $\sin kr_0$, for arbitrary k, is the analog of the function $\tilde{u}_k(r_0)$ in the Hartree-Fock approximation before orthogonalization. The function $u_k(r_0)$ is then the orthogonalized form of $\tilde{u}_k$ and, as discussed in Sec. II, it can be substituted in (3.5a) without changing Ψ_-.

In this context, it should be mentioned that in the work of Mittleman and Watson,[8] which concerns the construction of equivalent one-body potentials in the case that an incoming particle is different from the particles in the target, the functions for which the potentials are constructed are equivalent to those defined in (1.2).

We shall conclude with an example of a nontrivial method in which the phase shift is determined by a procedure different from any of those discussed above. It has been shown[9] that the s-wave scattering of electrons by hydrogen can be described in zeroth order (which approximation nevertheless can be expected to give results correct to within 25%) by the equation

$$\left[-\frac{\partial^2}{\partial r_<^2} - \frac{\partial^2}{\partial r_>^2} - \frac{2}{r_<} + 1 - k^2\right]\Psi_0^{(0)}(r_0,r_1) = 0. \quad (3.6)$$

$r_<$ is the lesser and $r_>$ is the greater of r_0 and r_1. [$\Psi_0^{(0)}$ is an approximation of (r_0r_1 times the) s-wave function

[7] M. Mittleman, University of California Radiation Lab. Rept. UCRL-5711 (1959) (unpublished).

[8] M. Mittleman and K. Watson, Phys. Rev. 113, 198 (1958).

[9] A. Temkin, Phys. Rev. Letters 4, 511 (1960).

of the $e-$H system.] The equation can be considered completely in the region $r_0>r_1$:

$$\left[-\frac{\partial^2}{\partial r_0^2}-\frac{\partial^2}{\partial r_1^2}-\frac{2}{r_1}+1-k^2\right]\Phi_0^{(0)}=0,\quad r_0>r_1,\quad (3.6a)$$

providing one adds the additional boundary condition corresponding to the triplet $\Psi_0^{(0)}$ that $\Phi_0^{(0)}$ be zero along the line $r_0=r_1$. $\Phi_0^{(0)}$ can be expanded in the form

$$\Phi_0^{(0)}(r_0,r_1)=\sin(kr_0+\delta)u_{10}(r_1)+\sum_{n=2}C_n e^{-\kappa_n r_0}u_{n0}(r_1),\quad (3.7)$$

where

$$\kappa_n=(1-n^{-2}-k^2)^{\frac{1}{2}}.$$

The $u_{n0}(r_1)$ are r_1 times the radial s state wave functions of the hydrogen atom. The sum includes the states of the continuum (for which $n\rightarrow i/p$, where p is the momentum of a continuous state). Each term is separately a solution of the above equation, thus obeying one of the boundary conditions of being 0 along $r_1=0$. The C_n and δ are determined by the remaining boundary condition $\Phi_0^{(0)}(r_0=r_1)=0$. In actual practice, we use a finite number of terms and determine the C_n and δ by minimizing the expression $\int_0^\infty|\Phi_0^{(0)}(r_0=r_1)|^2dr_0$. The minimization leads in the case that we only include the first two terms of (3.7) to the expressions

$$\tan 2\delta=\frac{-\int_0^\infty e^{-2\kappa_2 r}u_{20}^2dr\int_0^\infty \sin 2kr u_{10}^2dr+2\mathfrak{N}_s\mathfrak{N}_c}{\int_0^\infty e^{-2\kappa_2 r}u_{20}^2dr\int_0^\infty \cos 2kr u_{10}^2dr+\mathfrak{N}_s^2-\mathfrak{N}_c^2},$$

and

$$C_2=\frac{-\int_0^\infty \sin(kr+\delta)e^{-\kappa_2 r}u_{10}u_{20}dr}{\int_0^\infty e^{-2\kappa_2 r}u_{20}^2dr}.$$

Here

$$\mathfrak{N}_{(s;c)}=\int_0^\infty\begin{Bmatrix}\sin kr\\ \cos kr\end{Bmatrix}e^{-(\kappa_2+\frac{1}{2})r}u_{10}u_{20}dr.$$

The integrations are trivial, and one can select the correct quadrant of 2δ by testing to see which 2δ actually minimizes $\int_0^\infty|\Phi_0^{(0)}|^2dr$. This uniquely determines C_2.

At this point δ is still undetermined modulo π, and we would expect to use (1.2) to make δ unique. However,

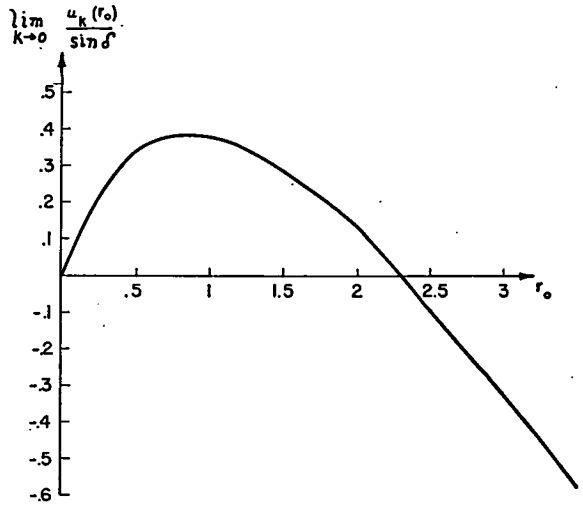

FIG. 3. Zero energy form of u_k given in (3.8), where $\Phi_0^{(0)}$ is given by (3.9) and (3.7). Only two terms in (3.7) are used. The function $\lim k\rightarrow 0$ $(\sin\delta)^{-1}u_k(r_0)$ is plotted. It is orthogonal to $u_{1s}(r_0)=2r_0e^{-r_0}$.

to use (1.2), which reduces here to

$$u_k(r_0)=\int_0^\infty u_{10}(r_1)\Psi_0^{(0)}(r_0,r_1)dr_1,\quad (3.8)$$

one must know how $\Psi_0^{(0)}$ is related to $\Phi_0^{(0)}$. This is not completely obvious since if $\Phi_0^{(0)}(r_0,r_1)$ is a solution of (3.6) in the region $r_0>r_1$, then the two solutions $\pm\Phi_0^{(0)}(r_1,r_0)$ are solution of (3.6) in the region $r_1>r_0$. Physically, it is obvious that if $\Psi_0^{(0)}$ is to correspond to the space antisymmetric (triplet) solution

$$\Psi_0^{(0)}(r_0,r_1)=-\Psi_0^{(0)}(r_1,r_0),$$

then $\Psi_0^{(0)}$ must be the combination

$$\begin{aligned}\Psi_0^{(0)}&=\Phi_0^{(0)}(r_0,r_1)\qquad r_0>r_1\\ &=-\Phi_0^{(0)}(r_1,r_0)\quad r_0<r_1.\end{aligned}\quad (3.9)$$

With this, the function $\Psi_0^{(0)}$ is completely defined and the integration (3.8) can be carried out from which δ can be found uniquely. On using the two term approximation of $\Phi_0^{(0)}$, we get the curve of Fig. 3, from which it is clear that $\delta\rightarrow\pi$.

ACKNOWLEDGMENTS

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