PHASE SHIFTS AND THE QUANTUM MECHANICAL HAMILTON-JACOBI EQUATION*

by

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ABSTRACT

20624

A method of obtaining absolute phase shifts by integration of the quantum mechanical Hamilton-Jacobi equation is developed and applied to the example of particles interacting through a Lennard-Jones potential. A new expression for the absolute phase shift is obtained in terms of an irregular solution of the Schroedinger equation.

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A numerical method of determining phase shifts may be based on the fact that although the wave function of a system may vary rapidly with the separation distance between the particles, the real and imaginary parts of the Hamilton-Jacobi representation of the wave function are slowly varying functions of the separation except in the region of a turning point. Using this fact, one may often use large step sizes in the integrations and thereby evaluate the phase shifts expeditiously.

In the present development as in the W.K.B. approach, the Ricatti substitution is made to obtain the quantum mechanical Hamilton-Jacobi equation[1] for the function $S(r^*)$. The function $S(r^*)$ has both real and imaginary parts corresponding to the phase and amplitude of the wave function, respectively. In the asymptotic region, the wave function is described by the W.K.B. approximation and one may use this as a first approximation in starting the computation. However, once the computation is started, the exact equations are used so that the resulting solution is equivalent to that obtained by solving the original Schroedinger equation. The solution corresponding to a satisfactory wave function must vanish at the origin. This suffices to determine one of the two arbitrary constants in the solution; the remaining constant fixes the normalization. The absolute phase shifts are

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1. The substitution $U(r^*) = e^{iS(r^*)/\Lambda^*}$ is quite general and the resulting equation for $S(r^*)$ is termed a "Ricatti equation". See, e.g., Birkhoff and Rota, Ordinary Differential Equations (Ginn, Boston, 1962).

then determined from the asymptotic form of the wave function.

1. The quantum mechanical Hamilton-Jacobi equation and the phase shifts

We restrict our attention to the scattering of two structureless particles interacting through a central potential. This process may be described by considering an equivalent single particle of reduced mass m scattered by a fixed center of force. The potential of interaction is taken to be of the form

$$\varphi(r) = \epsilon f(r/\sigma) \tag{1}$$

where the $f(r^*)$ is defined in the usual manner, so that the potential is zero at $r = \sigma$ and has a minimum value of $-\epsilon$. The radial Schroedinger equation describing the scattering process may be written in the form[2]

$$\frac{d^2u_l}{dr^{*2}} + \left\{\kappa^{*2} - \frac{l(l+1)}{r^{*2}} - \frac{4\pi^2}{\Lambda^{*2}} f(r^*)\right\} u_l(r^*) = 0 \tag{2}$$

where l is the angular momentum quantum number; r^* is the separation distance in reduced units

$$r^* = r/\sigma \quad ; \tag{3}$$

κ^* is the reduced wave number

$$\kappa^* = \kappa\sigma = \sigma\sqrt{2mE}/\hbar \tag{4}$$

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2. Hirschfelder, Curtiss and Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York 1954), 680.

where E is the energy and $\hbar$ is the Dirac constant; and

$$\Lambda^* = \hbar/(\sigma\sqrt{2mE}) \tag{5}$$

is the deBoer quantum parameter. It is convenient, in addition, to define a reduced effective potential as

$$\tilde{f}(r^*) = f(r^*) + l(l+1)\Lambda^{*2}/(4\pi^2 r^{*2}) \tag{6}$$

so that Eq. 2 becomes

$$\frac{d^2u_l}{dr^{*2}} + \left\{\varkappa^{*2} - 4\pi^2\tilde{f}(r^*)/\Lambda^{*2}\right\}u_l(r^*) = 0. \tag{7}$$

If $f(r^*)$ is zero, the functions u_l are closely related to the Bessel functions and asymptotically approach

$$A_l \sin(\varkappa^* r^* - l\pi/2) . \tag{8}$$

When $f(r^*)$ is not zero but approaches zero at large separations faster than r^{*-2}, the function u_l differs asymptotically from eq. 8 and approaches the function

$$C_l \sin(\varkappa^* r^* - l\pi/2 + \eta_l) \tag{9}$$

where η_l is a constant known as the phase shift. The differential cross section may be expressed in terms of the η_l.

a) The Hamilton-Jacobi equation

Let

$$u_\ell = e^{i S(n^*)/\Lambda^*} , \tag{10}$$

where $S(n^*)$ is a complex function. We obtain an equation for $S(n^*)$ by substitution of this form into Eq. 4. The resulting equation is

$$i\Lambda^* S''(n^*) - \{S'(n^*)\}^2 + 4\pi^2\{E^* - \tilde{f}(n^*)\} = 0 \tag{11}$$

where E^* is the reduced energy,

$$E^* = \mathcal{H}^{*2}\Lambda^{*2}/(4\pi^2) = E/\epsilon . \tag{12}$$

In the limit $\Lambda^* \to 0$, for fixed E^* and a fixed value of $\ell(\ell+1)\Lambda^{*2}$, $S(n^*)$ satisfies the equation

$$\{S'(n^*)\}^2 = 4\pi^2\{E^* - \tilde{f}(n^*)\} . \tag{13}$$

It is clear from Eq. 13 that, in this limit, $S(n^*)$ is purely real in the classical region and purely imaginary in the non-classical region. Eq. 13 is the classical Hamilton-Jacobi equation for Hamilton's characteristic function.[3]

Returning to Eq. 11, we set

$$S(n^*) = S_1(n^*) + i S_2(n^*) \tag{14}$$

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3. H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, Mass., 1959).

where $S_1(n^*)$ and $S_2(n^*)$ are real functions. The coupled equations for these two functions are then[4]

$$\Lambda^* S_1'' - 2 S_1' S_2' = 0 \tag{15}$$

and

$$(S_2')^2 - (S_1')^2 - \Lambda^* S_2'' + 4\pi^2 \{E^* - \tilde{f}(n^*)\} = 0 \, . \tag{16}$$

This pair of coupled second order equations are easily transformed into a set of four first order equations. Thus one obtains the set

$$S_1' = y_1 \tag{17}$$

$$S_2' = y_2 \tag{18}$$

$$\Lambda^* y_1' = 2 y_1 y_2 \tag{19}$$

$$\Lambda^* y_2' = y_2^2 - y_1^2 + 4\pi^2 \{E^* - \tilde{f}(n^*)\} . \tag{20}$$

These equations are completely equivalent to the original Schroedinger equation. Clearly, since the last two equations are uncoupled from the first two, they may be solved independently and the resulting solutions integrated to obtain $S_1(n^*)$ and $S_2(n^*)$.

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4. A set of related equations is treated in a different fashion by J. A. Wheeler, Phys. Rev. 52, 1123 (1937).

b. The asymtotic solution

In the numerical solution of these equations, it is convenient to begin the integration at a large value of ρ^* and integrate toward the origin. For this purpose, it is necessary to consider the asymptotic behavior of the four functions. From Eq. 9, it follows that asymptotically u_ℓ may also be written as a linear combination of $e^{i\kappa^*\rho^*}$ and $e^{-i\kappa^*\rho^*}$. Comparing these functions with the defining equation for $S(\rho^*)$, Eq. 14, we conclude that solutions exist such that S_2 approaches a constant for large ρ^* and S_1 approaches $\pm \kappa^*\Lambda^*\rho^* = \pm 2\pi\sqrt{E^*}\rho^*$. It then follows from Eqs. 17 and 18 that for these solutions

$$y_2 \rightarrow 0 \tag{21}$$

and

$$y_1 \rightarrow \pm 2\pi\sqrt{E^*} \quad . \tag{22}$$

The W.K.B. series solution of the equations gives more accurate asymptotic forms of the functions. This series solution is obtained by developing y_1 as a power series in Λ^* for fixed values of E^* and $\ell(\ell+1)\Lambda^{*2}$,

$$y_1 = \sum_{m=0}^{\infty} y_1^{(m)} \Lambda^{*m} \quad . \tag{23}$$

If this series is substituted into Eq. 19, we obtain y_2 as a series in Λ^* :

$$y_2 = \sum_{m=1}^{\infty} y_2^{(m)} \Lambda^{*m} \tag{24}$$

where

$$y_2^{(1)} = y_1^{(0)\prime} / 2 y_1^{(0)} \quad , \tag{25}$$

$$y_2^{(2)} = y_1^{(1)\prime} / (2 y_1^{(0)}) - y_1^{(0)\prime} y_1^{(1)} / (2 y_1^{(0)2}) , \tag{26}$$

. . .

On substituting these series expressions for y_1 and y_2 into Eq. 20, we find that

$$y_1^{(0)} = \pm \sqrt{4\pi^2 (E^* - \tilde{f}(n^*))} \tag{27}$$

and

$$y_2^{(1)} = -4\pi^2 \tilde{f}'(n^*) / (16\pi^2 (E^* - \tilde{f}(n^*))) \quad . \tag{28}$$

Eq. 27 is the classical limit since it is the zeroth term in the expansion in powers of Λ^* . In this limit, y_2 is zero. These results are consistent with Eq. 13, the classical limit of Eq. 11. The higher terms in the series, Eqs. 23 and 24, are quantum corrections.

c) The boundary condition at the origin.

The numerical solution of the equations is started at a value of ρ^* sufficiently large that Eqs. 27 and 28 represent the functions to a good approximation. This value of ρ^* is denoted as ρ_o^*. It follows from Eqs. 13 and 14 that a solution of these equations remains a solution if $S_1(\rho^*)$ and $S_2(\rho^*)$ are changed by adding arbitrary constants. The arbitrary additive constant on $S_1(\rho^*)$ is associated with the arbitrary phase of a solution (which is not necessarily well-behaved at the origin) and the arbitrary additive constant of $S_2(\rho^*)$ is associated with the arbitrary normalization of the wave function. For numerical convenience, we set

$$S_1(\rho_o^*) = S_2(\rho_o^*) = 0 \quad . \tag{29}$$

The solution of the equations representing a wave function which is well-behaved at the origin is formed from two numerical solutions. Since the Hamiltonian operator is real, it is easily shown that the real and imaginary parts of a solution are separately solutions of the equation. From this it follows that the complex conjugate of a solution is also a solution and furthermore, if the function is not purely real (or purely imaginary), the complex conjugate is an independent solution.[5] Thus, if

$$u_\ell = e^{i\{S_1(\rho^*) + i S_2(\rho^*)\}/\Lambda^*} \tag{30}$$

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5. This is equivalent to saying that the real and imaginary parts of a solution are themselves independent solutions.

is a solution, then

$$u_2^* = e^{-i\{S_1(n^*) - i S_2(n^*)\}/\Lambda^*} \tag{31}$$

is an independent solution. This result is easily shown to be consistent with Eqs. 19 and 20. Clearly, if $S_1(n^*)$, $S_2(n^*)$ is a solution of these equations, $-S_1(n^*)$, $S_2(n^*)$ is also a solution. If the first solution is obtained using as the asymptotic form, Eqs. 27 and 28, with the upper sign for $y_1^{(0)}$, the second solution would result from using the lower sign.

From the arguments just given it follows that the general solution of the Schroedinger equation, Eq. 7, may be written as

$$u = A_1 e^{iS_1(n^*)/\Lambda^*} e^{-S_2(n^*)/\Lambda^*} + A_2 e^{-iS_1(n^*)/\Lambda^*} e^{-S_2(n^*)/\Lambda^*} , \tag{32}$$

where A_1 and A_2 are arbitrary constants and $S_1(n^*)$ and $S_2(n^*)$ are solutions given asymtotically by Eqs. 21 and 22, with the upper sign. The condition that the wave function vanish at the origin is

$$u(0) = 0 = A_1 e^{iS_1(0)/\Lambda^*} e^{-S_2(0)/\Lambda^*} + A_2 e^{-iS_1(0)/\Lambda^*} e^{-S_2(0)/\Lambda^*} . \tag{33}$$

Thus,

$$A_1/A_2 = -e^{-2iS_1(0)/\Lambda^*} . \tag{34}$$

Using this relation between A_1 and A_2, we find that the well-behaved solution is

$$u(\pi^*) = A_1 e^{-S_2(\pi^*)/\Lambda^*}\left\{ e^{iS_1(\pi^*)/\Lambda^*} - e^{-iS_1(\pi^*)/\Lambda^*} e^{2iS_1(0)/\Lambda^*}\right\}. \quad (35)$$

The coefficient A_1 is determined by the normalization.

From the definition of y_1, Eq. 17, and the condition that $S_1(\pi_0^*) = 0$, it follows that

$$S_1(\pi^*) = \int_{\pi_0^*}^{\pi^*} y_1 \, d\pi^* \quad . \quad (36)$$

It is convenient to rewrite this result in the form

$$S_1(\pi^*) = 2\pi\sqrt{E^*}\,(\pi^* - \pi_0^*) + \int_{\pi_0^*}^{\pi^*} (y_1 - 2\pi\sqrt{E^*})\, d\pi^* \quad . \quad (37)$$

Since the numerical solution is based on the use of the upper sign in the initial condition, Eq. 27, the integral in the last expression converges in the limit $\pi^* \to \infty$. Thus, the solution given by Eq. 35 is asymptotically of the form

$$u(\pi^*) = A_1 e^{-S_2(\infty)/\Lambda^*} e^{i\mathcal{H}^*(\pi^* - \pi_0^*)} e^{i\int_{\pi_0^*}^{\infty} (y_1 - 2\pi\sqrt{E^*})\, d\pi^*/\Lambda^*}$$

$$- A_1 e^{-S_2(\infty)/\Lambda^*} e^{2iS_1(0)/\Lambda^*} e^{-i\mathcal{H}^*(\pi^* - \pi_0^*)} e^{-i\int_{\pi_0^*}^{\infty} (y_1 - 2\pi\sqrt{E^*})\, d\pi^*/\Lambda^*} \quad . \quad (38)$$

Comparing this expression with the equation defining the phase shift, Eq. 9, we find that

$$\eta_\ell = (N + \ell/2)\pi - \varkappa^* \rho_0^* - S_1(0)/\Lambda^* + (1/\Lambda^*)\int_{\rho_0^*}^{\infty} (y_1 - 2\pi\sqrt{E^*})\, d\rho^* \quad (39)$$

where N is an arbitrary integer.

d) The absolute phase shift

It is of interest to note that the last expression for the phase shift may be rewritten in the form

$$\eta_\ell = (N + \ell/2)\pi + (1/\Lambda^*)\int_0^{\infty} (y_1 - 2\pi\sqrt{E^*})\, d\rho^* . \quad (40)$$

In this form, it is clear that the result is independent of the choice of ρ_0^* and the convention that $S_1(\rho_0^*) = 0$.

We evaluate the integer N by considering a potential

$$f(\rho^*) = \lambda F(\rho^*) \quad (41)$$

where λ is a coupling parameter which may be varied continuously. From continuity considerations, it follows that N cannot depend on λ or the energy E^* . Using the definition of y_1 , Eq. 17, Eq. 40 may be written as

$$\eta_\ell = (N + \ell/2)\pi + (1/\Lambda^*) \lim_{\rho^* \to \infty} \{ S_1(\rho^*) - S_1(0) - \chi \} \quad (42)$$

where

$$\chi = 2\pi\sqrt{E^*}\, \rho^*/\Lambda^* \quad . \quad (43)$$

The phase shift η_ℓ is defined in such a manner that as $\lambda \to 0$, $\eta_\ell \to 0$. For this value of λ, the solution of the Schroedinger equation corresponding to Eq. 30 is simply related to the first Hankel function $h_\ell^{(1)}(x)$, i.e.

$$x\, h_\ell^{(1)}(x) = x\{ j_\ell(x) + i\, n_\ell(x)\} = e^{-S_2(\pi^*)/\Lambda^*}\, e^{i S_1(\pi^*)/\Lambda^*}, \quad (44)$$

where $j_\ell(x)$ and $n_\ell(x)$ are the spherical Bessel and Neumann functions. This function has the asymptotic form[6]

$$x\, h_\ell^{(1)}(x) \longrightarrow e^{i(x - \ell\pi/2 - \pi/2)}. \quad (45)$$

If, for the present, therefore, we restrict $S_1(0)/\Lambda^*$ to lie in the range

$$-\pi < S_1(0)/\Lambda^* < \pi \quad (46)$$

it follows from the form of $x\, h_\ell^{(1)}(x)$ in the limit $x \to 0$ [6], that

$$S_1(0)/\Lambda^* = -\pi/2. \quad (47)$$

It follows from Eq. 42 that the restriction, Eq. 46, does not affect the result since only the difference between $S_1(\pi^*)/\Lambda^*$ and $S_1(0)/\Lambda^*$ is important, and thus the ambiguity associated with Eq. 47 may be

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6. Morse and Feshbach, Methods of Theoretical Physics (McGraw-Hill, New York, 1953).

ignored.

It follows from Eqs. 19 and 20 that

$$y_1 \neq 0 \tag{48}$$

except at a singularity of the Schroedinger equation. Therefore, since

$$y_1(\rho_0^*) > 0 \quad , \tag{49}$$

$S_1(\rho^*)$ is a monotone increasing function of ρ^*. From the form of Eq. 44, it follows that whenever $\eta_\ell(x)$ is zero, S_1/Λ^* is an integer multiple of π. Thus, as $\eta_\ell(x)$ goes through successive nodes, S_1/Λ^* increases by π as illustrated in Fig. 1. For m sufficiently large the position of the m th node is[7]

$$x_m = (\ell + 2m)\pi/2 - \pi/2 \; ; m \to \infty. \tag{50}$$

Thus,

$$S_1(\rho_m)/\Lambda^* = (m-1)\pi \quad . \tag{51}$$

When these results are substituted into Eq. 42, one obtains

$$N = 0 \tag{52}$$

as the condition on N such that η_ℓ be an absolute phase shift.

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7. Jahnke and Emde, Tables of Functions (Dover Publications, New York, 1945).

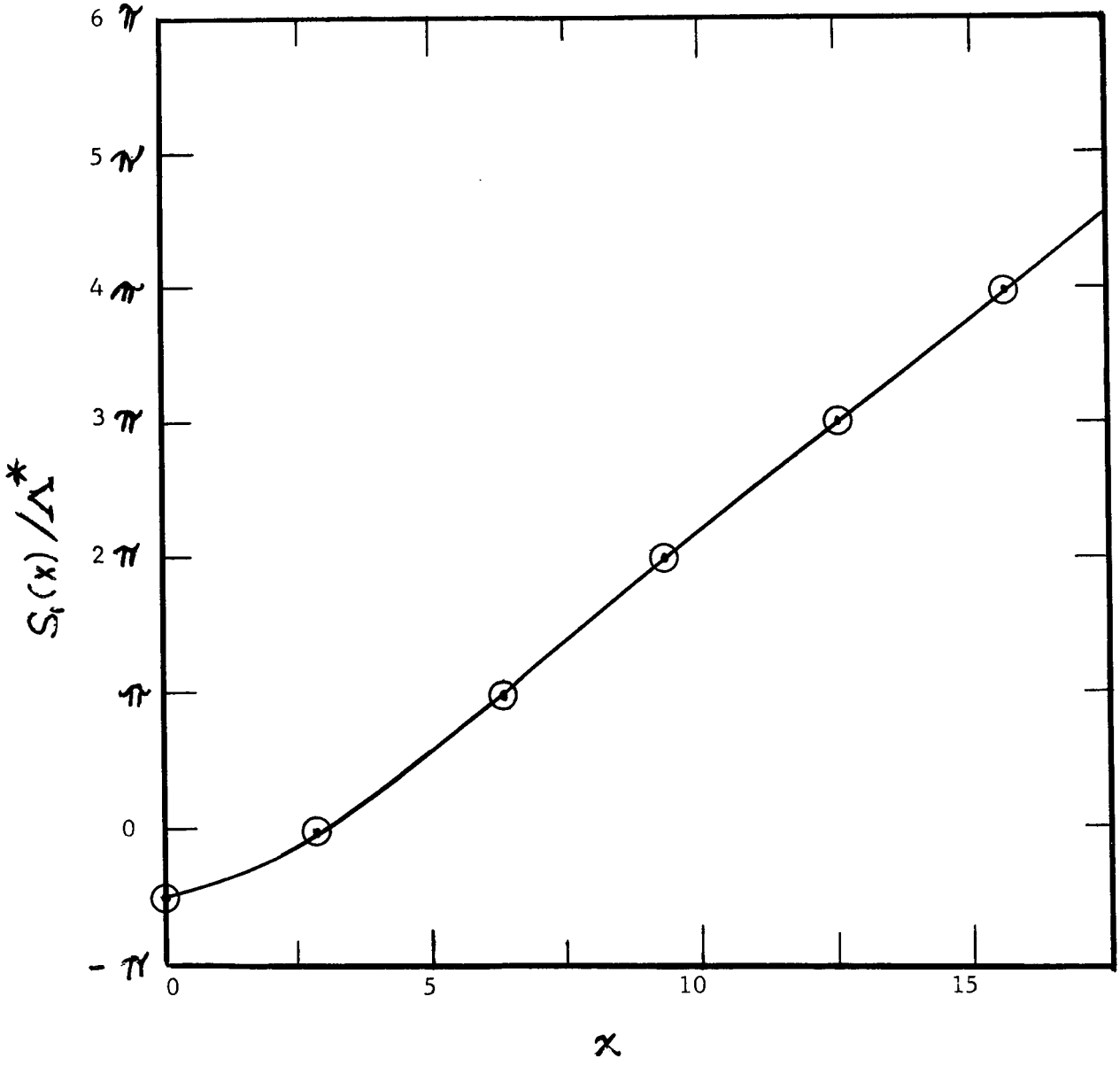

Fig. 1

From Eq. 40 it follows that

$$\eta_\ell = (1/\Lambda^*) \int_0^\infty (y_\ell - y_\ell^B)\, d\rho^* \qquad (53)$$

where the superscript B implies that $f(\rho^*) = 0$. This result gives the absolute phase shift in terms of the difference in the phase at the origin of irregular solutions of the Schroedinger equation which are asymptotically proportional to $h_\ell^{(1)}(\chi)$.

e) The correction term

Since ρ_0^* is taken to be sufficiently large that the first W.K.B. approximation holds for $\rho^* > \rho_0^*$, we may use Eq. 27 to evaluate the integral in Eq. 39. In the asymptotic region the potential is small compared to the energy E^* . Thus the function may be further approximated by the series

$$y_\ell \cong 2\pi\sqrt{E^*} - \pi \tilde{f}(\rho^*)/\sqrt{E^*} + \pi(\tilde{f}(\rho^*))^2/4E^{*3/2} - (3\pi/24)(\tilde{f}(\rho^*))^3/E^{*5/2} + \ldots \qquad (54)$$

With this series and an explicit form of the potential function the integral correction term in the expression for the phase shift, Eq. 39, may be evaluated. The numerical applications discussed later are based on the Lennard-Jones form of the potential function

$$f(\rho^*) = 4\left(1/\rho^{*12} - 1/\rho^{*6}\right) . \qquad (55)$$

For this case, one obtains the explicit expression (to terms of order $(\eta_0^*)^{-6}$)

$$\eta_l = l\pi/2 - S_1(0)/\Lambda^* - 2\pi\sqrt{E^*}\,\eta_0^*/\Lambda^* - l(l+1)\Lambda^*/4\pi\sqrt{E^*}\eta_0^*$$

$$+ \left\{ 4\pi/5\Lambda^*\sqrt{E^*} - l^3(l+1)^3\Lambda^{*5}/2^9\pi^5 E^{*5/2}\,5 \right\}/\eta_0^{*5} \qquad (56)$$

$$+ l^2(l+1)^2\Lambda^{*3}/3E^{*3/2}\,2^6\pi^3\eta_0^{*3} \,.$$

It is this expression which is evaluated to obtain numerical values of the phase shifts.

2. Numerical Techniques

The problem of determining the phase shifts has been reduced in the previous section to that of solving the coupled differential equations, Eqs. 17 to 20. The numerical solution is carried from a large value of η^*, denoted η_0^*, in the direction of decreasing η^*. At the initial point, η_0^*, $S_1 = S_2 = 0$ and y_1 and y_2 are given by Eqs. 23, 24, 27 and 28 with the choice of the upper sign in Eq. 27. In the numerical examples, only the first non-zero terms in the series approximations were used.

a) The difference equations.

The pair of equations for y_1 and y_2, Eqs. 19 and 20, are of a type known as "stiff equations".[8] These equations are

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8. J. O. Hirschfelder, "Applied Mathematics as used in Theoretical Chemistry, Proc. of Symposia in Applied Math., vol. XV, Amer. Math. Soc. (1963); also Curtiss and Hirschfelder, Proc. of Nat. Acad. Sci., 235 (1952).

characterized by extreme stability with respect to solution in one direction, in this case in the direction of decreasing r^*. The property generally occurs when the derivative is multiplied by a numerically small coefficient. Thus these equations become "stiffer" as $\Lambda^* \to 0$, the condition that the W.K.B. method be applicable.

Thus the numerical solution of these equations is started by estimating the values of y_1 and y_2 by the W.K.B. approximation, Eqs. 27 and 28. Then the full equations, Eqs. 17 to 20, are used to continue the solution toward the origin. To do this, backward difference methods are used to estimate y_2^2 and y_2' at the point r_i^* in terms of the previous values of y_2. This is equivalent to correcting the W.K.B. approximation for y_1 by including effects due to y_2 and y_2'. The resulting difference equation is

$$y_1(r_i^*) = +\sqrt{\begin{array}{l} 4\pi^2(E^* - \tilde{f}(r_i^*)) \\ +\{2y_2(r_{i-1}^*) - y_2(r_{i-2}^*)\}^2 \\ -(\Lambda^*/\Delta)\{y_2(r_{i-1}^*) - y_2(r_{i-2}^*)\} \end{array}}, \quad (57)$$

where Δ is the increment in r^* - a negative value.

To obtain an expression for $y_2(r_i^*)$, Eq. 20 is differentiated implicitly to obtain an expression for y_1' which is substituted into Eq. 19. Then the derivatives of y_2 appearing in the expression for y_2 are again estimated by backward differences. The explicit expression for $y_2(r_i^*)$ is then

$$y_2(r_i^*) = \left[4y_1^2(r_i^*)\right]^{-1}\left[\begin{array}{l} \Lambda^* \tilde{f}'(r_i^*) + 2\Lambda^* y_2(r_{i-1}^*)\{y_2(r_{i-1}^*) - y_2(r_{i-2}^*)\}/\Delta \\ -\Lambda^{*2}\{y_2(r_{i-1}^*) - 2y_2(r_{i-2}^*) + y_2(r_{i-3}^*)\}/\Delta^2 \end{array}\right]. \quad (58)$$

The stability properties of these difference equations leads to a lower limit on the step size Δ which may be used. These stability properties of the difference equations are closely related to the "stiff" character of the differential equations. As the turning point is approached, the functions $y_1(n^*)$ and $y_2(n^*)$ begin to change more rapidly. The minimum step size required for stability then is no longer sufficiently small that the difference equations approximate sufficiently well the differential equations. At this point, the equations lose their stiff character and it is necessary to use an alternate numerical method.

b) The stability condition.

To investigate the stability of the difference equations we let the set $y_{1i}^{(0)}$ and $y_{2i}^{(0)}$ and the set y_{1i} and y_{2i} be two exact solutions of the difference equations, Eqs. 57 and 58. The perturbations z_{1i} and z_{2i} are defined by

$$y_{1i} = y_{1i}^{(0)} + z_{1i} \tag{59}$$

and

$$y_{2i} = y_{2i}^{(0)} + z_{2i} \tag{60}$$

If the solutions are stable the perturbations z_{1i} and z_{2i} decrease as i increases. To investigate the stability, the solutions, Eqs. 59 and 60, are substituted into the equations, Eqs. 57 and 58. Since the perturbations z_{1i} and z_{2i} are assumed to be small, the resulting equations are linearized. The

resulting pair of equations are

$$z_{1i} = \sum_{j=0}^{3} (\alpha_{11j} z_{1i-j} + \alpha_{12j} z_{2i-j}) , \tag{61}$$

$$z_{2i} = \sum_{j=0}^{3} (\alpha_{21j} z_{1i-j} + \alpha_{22j} z_{2i-j}) \tag{62}$$

where

$$\alpha_{11j} = 0 \quad \text{for all } j , \tag{63}$$

$$\alpha_{120} = 0 \tag{64}$$

$$\alpha_{121} = \left[2 y_{1i}^{(0)}\right]^{-1} \left[-\Lambda^*/\Delta + 4\left\{2 y_{2i-1}^{(0)} - y_{2i-2}^{(0)}\right\}\right] \tag{65}$$

$$\alpha_{122} = \left[2 y_{1i}^{(0)}\right]^{-1} \left[\Lambda^*/\Delta - 2\left\{2 y_{2i-1}^{(0)} - y_{2i-2}^{(0)}\right\}\right] \tag{66}$$

$$\alpha_{123} = 0 \tag{67}$$

$$\alpha_{210} = -2 y_{2i}^{(0)} \Lambda^* / y_{1i}^{(0)} \tag{68}$$

$$\alpha_{21j} = 0 \,, \quad j \neq 0 \tag{69}$$

$$\alpha_{220} = 0 \tag{70}$$

$$\alpha_{221} = \left[4 y_{ii}^{(0)2}\right]^{-1}\left[-\Lambda^{*2}/\Delta^2 + 2\Lambda^* y_{2i-1}^{(0)}/\Delta + 2\Lambda^*\{y_{2i-1}^{(0)} - y_{2i-2}^{(0)}\}/\Delta\right] \tag{71}$$

$$\alpha_{222} = \left[4 y_{ii}^{(0)2}\right]^{-1}\left[2\Lambda^{*2}/\Delta^2 - 2\Lambda^* y_{2i-1}^{(0)}/\Delta\right] \tag{72}$$

and

$$\alpha_{223} = -\Lambda^{*2}/\left[4 y_{ii}^{(0)2}\Delta^2\right] \,. \tag{73}$$

Clearly a solution of Eqs. 61 and 62 exists of the form

$$z_{1m} = A_1 e^{ma} \tag{74}$$

$$z_{2m} = A_2 e^{ma} \tag{75}$$

if a is a root of the determinental equation

$$\begin{vmatrix} \left(\sum_{j=0}^{3} \alpha_{11j} e^{-ja}\right) - 1 & \sum_{j=0}^{3} \alpha_{12j} e^{-ja} \\ \sum_{j=0}^{3} \alpha_{21j} e^{-ja} & \left(\sum_{j=0}^{3} \alpha_{22j} e^{-ja}\right) - 1 \end{vmatrix} = 0 \quad . \tag{76}$$

Defining

$$\xi = e^{-a} \quad , \tag{77}$$

we obtain the cubic equation for ξ ,

$$\beta_0 + \beta_1 \xi + \beta_2 \xi^2 + \beta_3 \xi^3 = 0 \tag{78}$$

where

$$\beta_0 = y_{1i}^{(o)2} \Delta^2 / \Lambda^{*2} \tag{79}$$

$$\beta_1 = \left[1/4 - \Delta y_{2i}^{(o)} / \Lambda^* + \Delta y_{2i-2}^{(o)} / 2\Lambda^* - \Delta y_{2i-1}^{(o)} / \Lambda^* + 8 y_{2i}^{(o)} \Delta^2 \left\{ y_{2i-1}^{(o)} - y_{2i-2}^{(o)} / 2 \right\} / \Lambda^* \right] \tag{80}$$

$$\beta_2 = \left[-1/2 + \Delta y_{2i}^{(o)} / \Lambda^* + \Delta y_{2i-1}^{(o)} / 2\Lambda^* - 4 y_{2i}^{(o)} \Delta^2 \left\{ y_{2i-1}^{(o)} - y_{2i-2}^{(o)} / 2 \right\} / \Lambda^* \right] \tag{81}$$

and

$$\beta_3 = 1/4 \quad . \tag{82}$$

Eq. 78 gives ξ as a function of Δ , Λ^* , $y^{(0)}_{1j}$ and $y^{(0)}_{2j}$ and from the form of the z_{1m} and z_{2m} , it follows that the difference equations are stable if

$$|\xi| > 1.0 \quad . \tag{83}$$

If we restrict our attention to n^* sufficiently far from the classical turning point, we may to a reasonable approximation neglect all terms in the $\beta's$ involving Δ , Λ^* and $y^{(0)}_{2j}$ and approximate Eq. 78 by

$$f(\xi) = \Delta^2 y^{(0)2}_{1i} / \Lambda^{*2} \tag{84}$$

where

$$f(\xi) = -\xi/4 + \xi^2/2 - \xi^3/4 \quad . \tag{85}$$

Clearly, we need consider only $f(\xi)>0$. The cubic function $f(\xi)$ is illustrated in Fig. 2. From this figure it is seen that if

$$\Delta^2 y^{(0)2}_{1i} / \Lambda^{*2} < 1 \quad , \tag{86}$$

the real root of Eq. 84 corresponds to an unstable solution. On the other hand, if

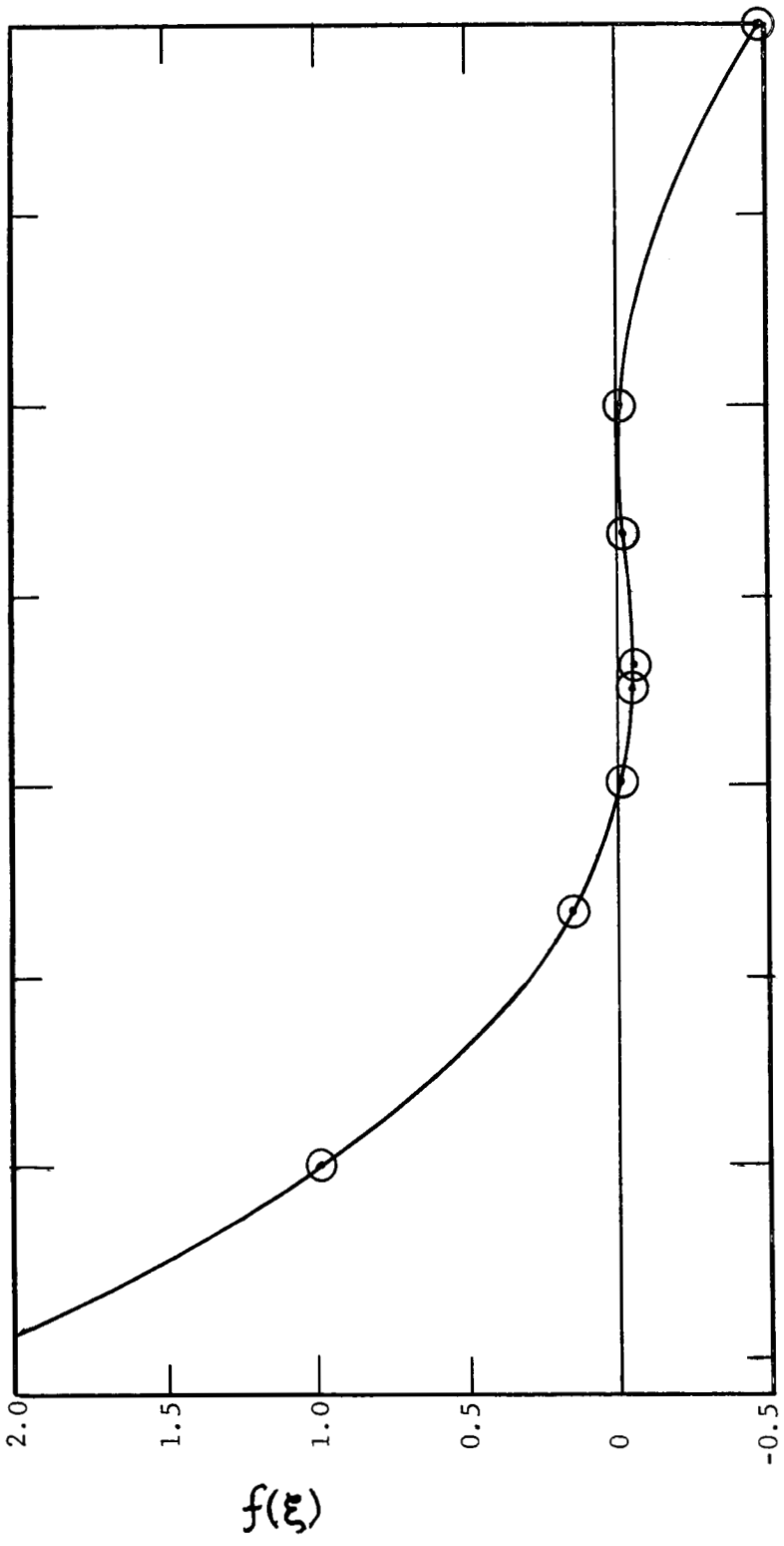

Fig. 2

$$\Delta^2 y_{ii}^{(o)2}/\Lambda^{*2} > 1 \quad , \tag{87}$$

the real root of Eq. 84 leads to a stable solution. It may be shown that if the condition, Eq. 87, holds, the complex roots of the cubic also satisfy the condition of stability. Thus, to the approximation being considered, the condition of stability is that

$$|\Delta| > \Lambda^*/|y_{ii}^{(o)}| \quad . \tag{88}$$

If Δ satisfies this condition, the z_{1m} and z_{2m} decrease as m increases. Clearly, it is possible to obtain a more exact stability criterion by obtaining a more accurate solution of Eq. 60.

c) The numerical solution

As the solution proceeds toward the turning point, $y_2(\pi^*)$ and $y_2'(\pi^*)$ become large and at some point Eqs. 15 and 16 become no longer "stiff". When this region is reached, an ordinary Runge-Kutta[9] technique may be used to solve the equations. This method may be used to complete the numerical solution of the equations.

3. The numerical results.

To illustrate the present numerical method of evaluating the phase shifts we present the following exploratory results. To carry out a numerical evaluation, it is necessary to choose four numerical parameters; a starting point π_0^*, an interval size in the stiff region Δ, a "join point" π_c^* at which the

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9. W. E. Milne, Numerical Solution of Differential Equations (John Wiley and Sons, New York, 1953).

difference equations are changed from the stiff form to the Runge-Kutta equations, and an interval size in the Runge-Kutta region, denoted by Δ_{RK}. In addition, values of three physical parameters must be chosen. These may be taken to be E^*, Λ^* and ℓ. In the present calculations, the function $f(n^*)$ is taken to be of the Lennard-Jones form, Eq. 55.

To investigate the effect of varying the numerical parameters, a number of calculations were made for[10]

$$E^* = 0.0228$$

$$\Lambda^* = 0.3158$$

and

$$\ell = 0.0$$

The resulting values of the phase shift are illustrated in Fig. 3. The values in Fig. 3 may be compared with Bernstein's value[10] of 2.551 obtained by direct integration of the Schroedinger equation using the Runge-Kutta method. These results indicate that for this case, the optimum values of the numerical parameters are n_0^* about 6.0, $|\Delta|$ greater than 0.25, Δ_{RK} between -0.01 and -0.0025 and n_c^* between 3.25 and 4.00. The functions $y_1(n^*)$, $y_2(n^*)$, $S_1(n^*)/\Lambda^*$ and $S_2(n^*)/\Lambda^*$ for $\ell = 0$, $E^* = 0.0228$ and $\Lambda^* = 0.3158$ are illustrated in Figs. 4-7.

It is of interest to point out that the stability condition,

10. These values correspond to Bernstein's A = 3, B = 125 and $\ell = 0$. See R. B. Bernstein, J. Chem. Phys. 33, 795-804 (1960).

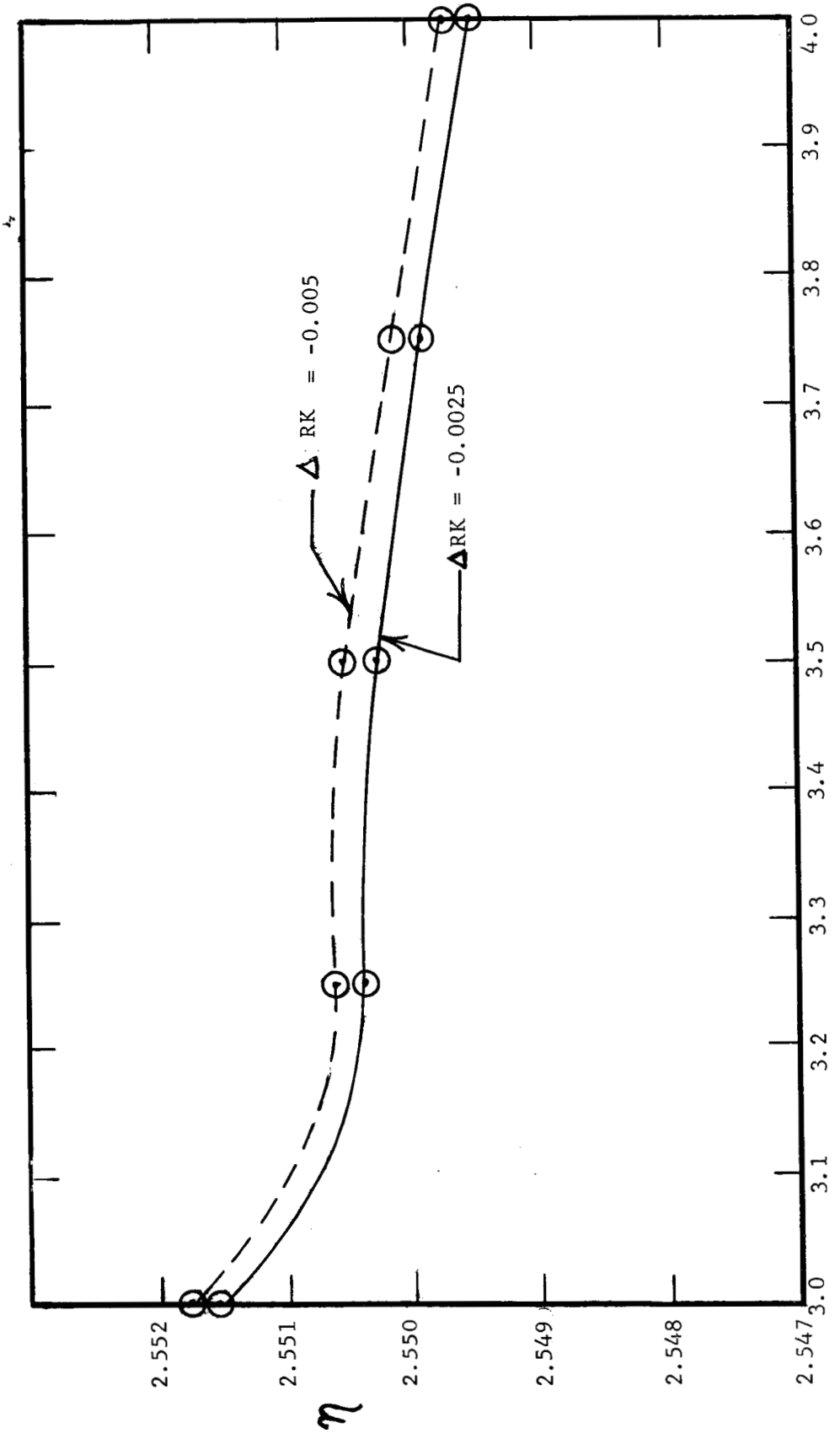
2.552
2.551
2.550
2.549
2.548
2.547
η
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
Δ RK = -0.005
ΔRK = -0.0025
η_c^*

Fig. 3

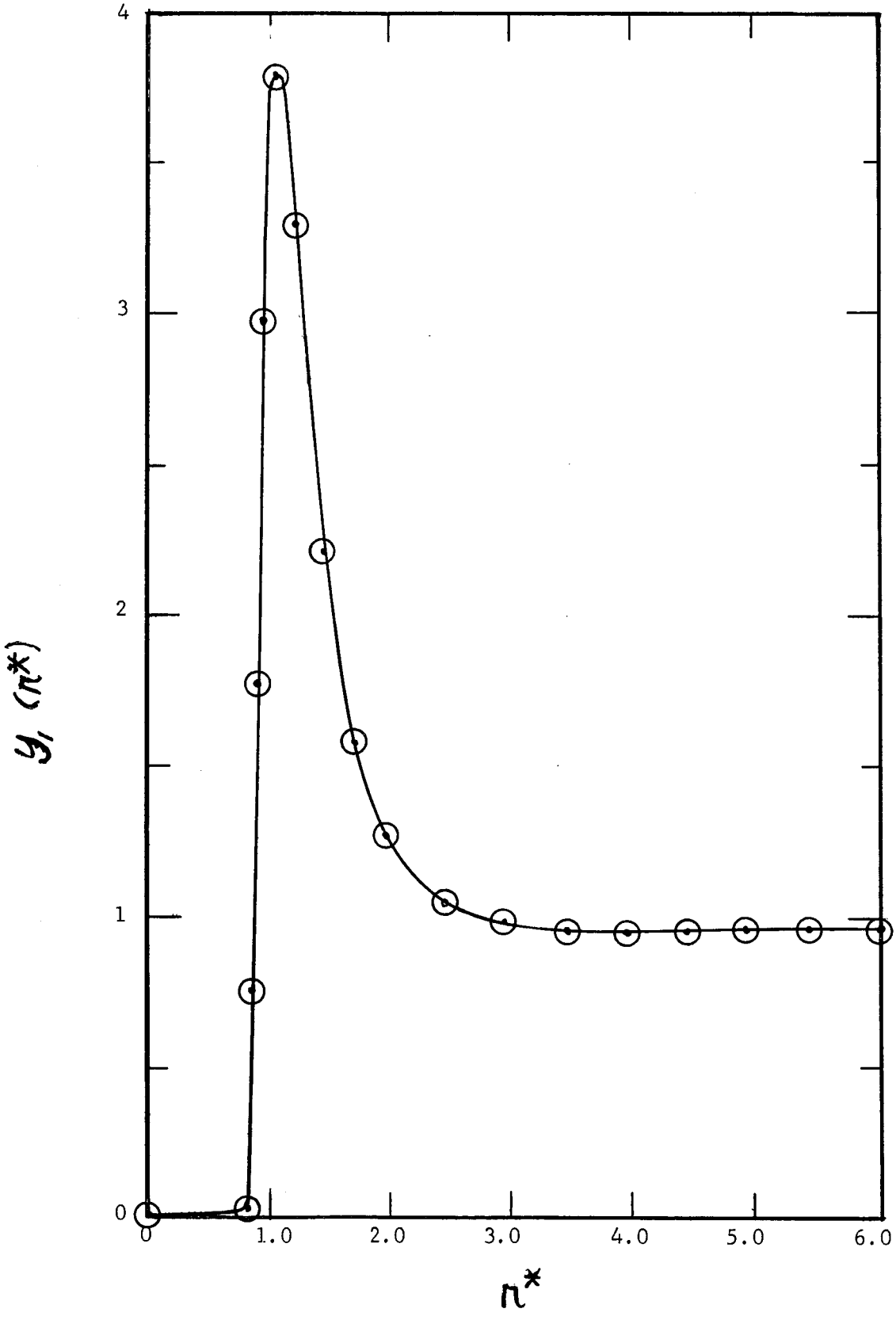

Fig. 4

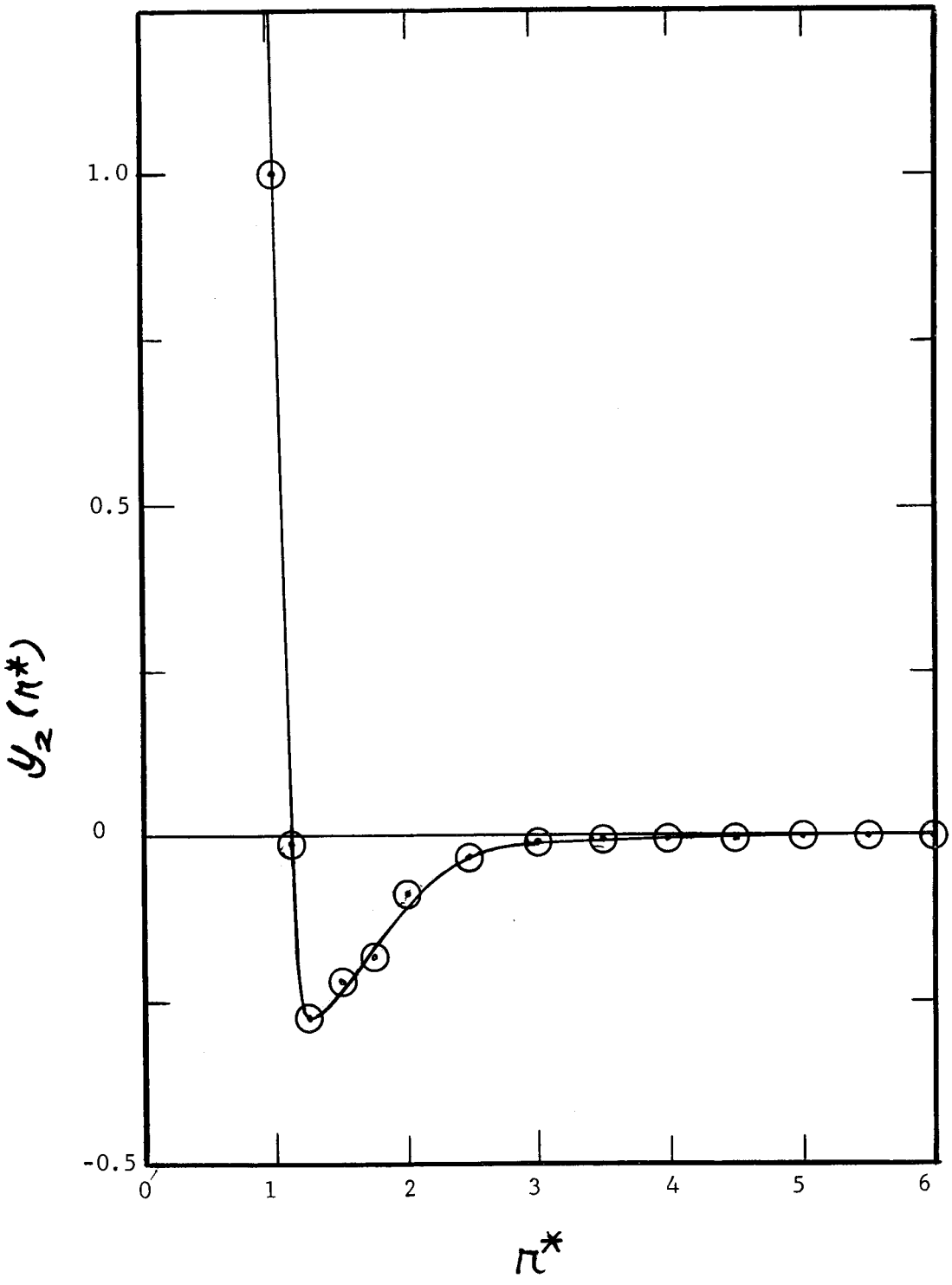

Fig. 5

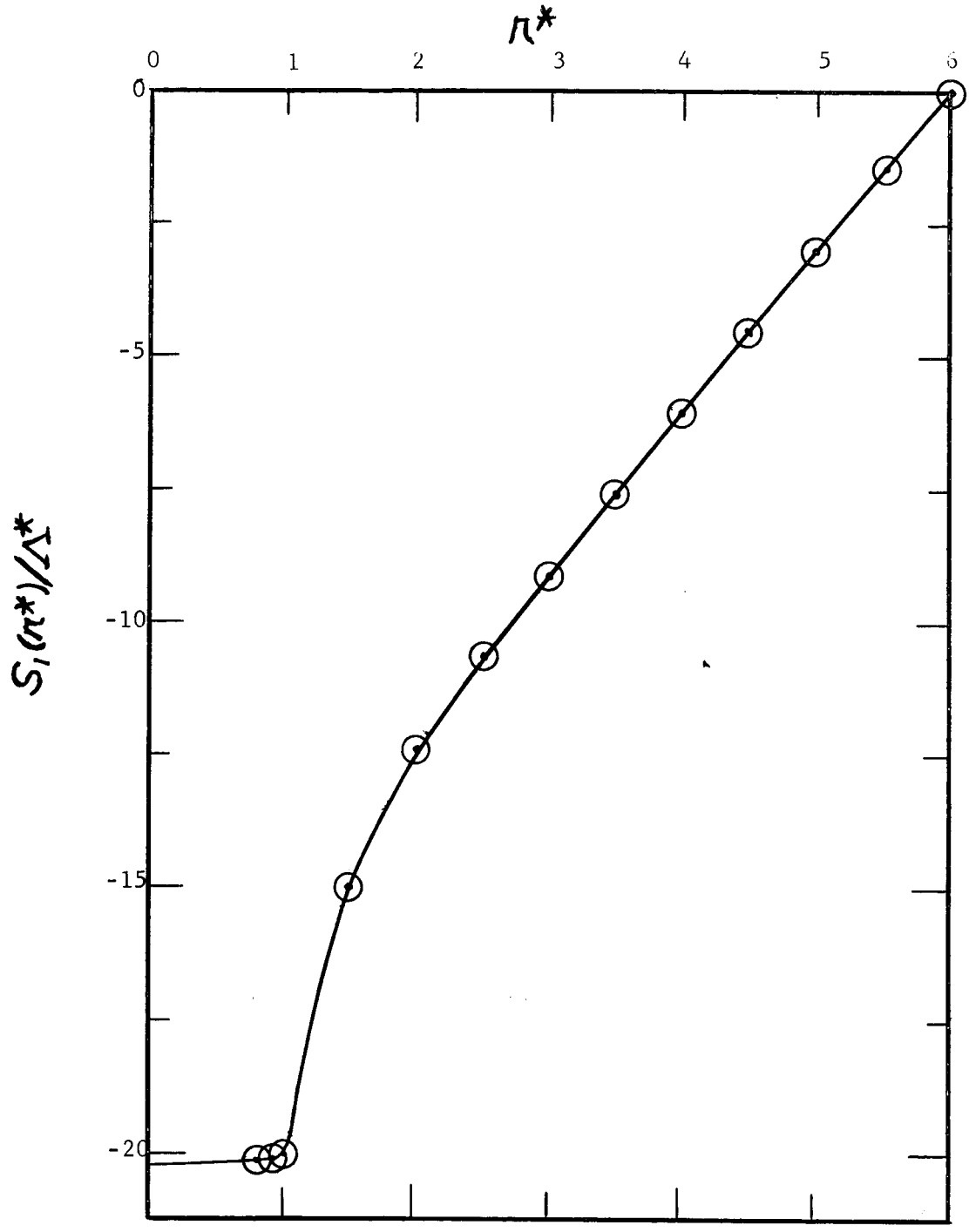

Fig. 6

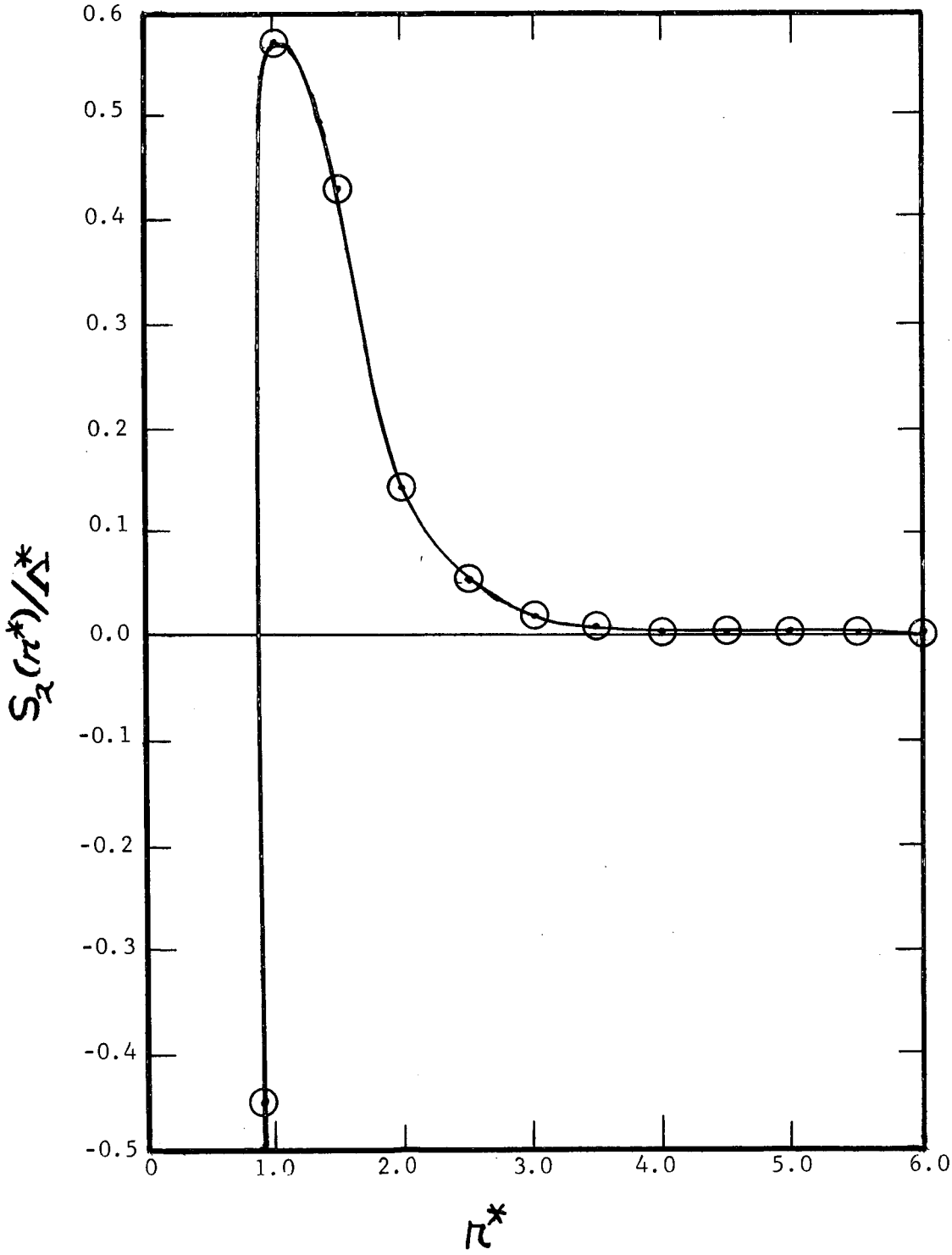

Fig. 7

Eq. 85, indicates that these calculations were made using an unstable value of Δ . However, the errors $\mathfrak{Z}_{1m}$ and $\mathfrak{Z}_{2m}$ due to the use of the W.K.B. approximation and round-off errors were small enough, and the number of steps few enough, that the accumulated error was not significant.

Table 1 gives values of the phase shift for $\ell = 0$, $\Lambda^* = 0.3158$ and four values of E^* all obtained using $\Delta = -.25$, $\Delta_{RK} = -.01$, $\pi_c^* = 3.25$, and $\pi_o^* = 6.0$; the results agree to the figures given with Bernstein's results.[10]

TABLE 1

Values of η_o are shown for four values of E^* when ℓ = 0, Λ^* = 0.3158.

E^*	.0228	.0628	.1238	.2046
η_o	2.551	-0.484	-3.140	-5.565

When ℓ is non-zero, it is possible to have one or three turning points. The results given in Table 2 are for ℓ = 15, Λ^* = 0.3158 and four values of E^* such that there is only one turning point. These results were obtained taking Δ = -0.25, and Δ_{RK} = -0.01 and the values of π_c^* and π_o^* indicated. The phase shift for E^* = 0.0628 is in poor

TABLE 2

$\eta_{15}(E^*)$ is shown for several E^*, Π_c^* and Π_o^*.

	E^*	0.2526	0.2046	0.1238	0.0628
Π_c^*	Π_o^*	$\eta_{15}(E^*)$	$\eta_{15}(E^*)$	$\eta_{15}(E^*)$	$\eta_{15}(E^*)$
3.00	10.0	3.806	3.214	0.489	-.008
3.00	15.0	3.804	3.211	0.484	-.020
3.50	10.0	3.806	3.215	0.489	+.078
3.50	15.0	3.804	3.212	0.484	+0.064
4.00	10.0	3.807	3.215	0.489	0.103
4.00	15.0	3.804	3.212	0.487	0.100
5.00	10.0	3.807	3.215	0.490	0.108
5.00	15.0	3.804	3.213	0.489	0.105
Reference [10]		3.805	3.212	0.490	0.110
All reference values have an uncertainty of $\pm$.002.					

agreement with that of Bernstein for $r_c^* < 4.00$, because the turning point occurs at a much larger value of r^*, (about $r^* = 3.0$), than for the other values of E^*.

The results[11] shown in Table 3 describe a series of calculations with constant values of E^* and $(l + 1/2)\Lambda^*$ and varying values of the quantum parameter, Λ^*. The conditions are such that there are three turning points. For $l > 60$, it is necessary to use a much smaller Δ_{RK} in order to follow the solution through the non-classical region, since as $\Lambda^* \to 0$, barrier penetration becomes difficult.

4. Conclusions

It is found that accurate values of the phase shifts may be obtained by integration of the quantum mechanical Hamilton-Jacobi equation. An advantage of this technique is that one deals with more slowly varying functions than the radial wave function. The application of the boundary condition that the wave function vanish at $r^* = 0$ is straightforward. Further, a new expression for the absolute phase shifts is obtained which may be useful in other applications. Further study of the method may result in methods of predicting the optimum values of the numerical parameters and increased efficiency of the method in the region of the turning point.

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11. These calculations repeat some unpublished results of S. Imam-Rahajoe, obtained with the computer program developed by Bernstein.

TABLE 3

Values of η are shown for $E^* = 0.4$ and $(\ell+1/2)\Lambda^* = 7.949$. Results were obtained using $\Delta = -0.25$, $\Delta_{RK} = -0.01$, $n_c^* = 3.25$, and $n_o^* = 10.0$.

		η	
ℓ	Λ^*	present results	ref. 11
10	0.75703	1.073	1.075
20	0.38775	4.366	4.368
40	0.19627	6.402	6.396
60	0.13139	10.935	10.790
100	0.07909	unstable	17.070

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