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SEMICLASSICAL PHASE SHIFTS FOR LOW ENERGY ORBITING COLLISIONS

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### Author

Herm, Ronald R.

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Ronald R. Herm

July 1967

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July, 1967

SEMICLASSICAL PHASE SHIFTS FOR  
LOW ENERGY "ORBITING" COLLISIONS

Ronald R. Herm†

Inorganic Materials Research Division  
Lawrence Radiation Laboratory  
and Department of Chemistry  
University of California  
Berkeley, California 94720

Abstract

A semiclassical expression for the phase shift in the literature which is applicable even when a maximum exists in the effective potential is re-expressed in terms of the simple JWKB phase integrals. This expression may be employed to calculate phase shifts from tables of reduced functions computed for a Lennard-Jones (12-6) potential. Sample semiclassical calculations are compared with published exact values; excellent qualitative and good quantitative agreement is obtained. Finally, the qualitative nature of the quantal corrections to the classical total and differential cross sections and the collision lifetime is discussed.

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## INTRODUCTION

In treating the elastic scattering of atoms or molecules subject to a spherically symmetric potential, a full partial wave quantum mechanical calculation can be prohibitively time consuming due to the large number of partial waves which contribute. On the other hand, the information concerning the intermolecular potential which is obtained from scattering experiments is often derived from the special quantal features which are observed.<sup>1</sup> It has proven possible to incorporate the quantal effects which have been observed into a modified classical scattering theory through the development of a semiclassical theory<sup>2</sup> employing the "JWKB" expression for the phase shift.<sup>3</sup> The validity of the JWKB expression has been examined by numerical comparison with the exact quantal solution.<sup>4-8</sup> In general, the JWKB approximation is very good,<sup>9</sup> although it must be modified for low incident energies where classically the phenomena of orbiting collisions is expected.<sup>6-8,10</sup>

The treatment given here begins by examining the classical expressions for the angle of deflection and collision

lifetime near an orbiting singularity. A semiclassical expression for the phase shift valid for incident energies near a maximum in the effective potential, previously derived by Ford, et. al.,<sup>11</sup> is then re-expressed in terms of the JWKB classical phase integrals with simple correction terms which incorporate the quantal features of tunnelling and the uncertainty principle. Table of reduced phase integrals computed for the Lennard-Jones (12 - 6) potential are given in the Appendix. Semiclassical phase shifts, readily calculated from these reduced Tables, are shown to be in excellent qualitative and good quantitative agreement with published values computed by solving Schrödinger's equation. Finally, possible experimental consequences of the special resonance features which appear in the phase shift are discussed semiclassically.

#### CLASSICAL ORBITING

A Lennard-Jones (12 - 6) potential is used throughout this paper to illustrate the procedure, but the methods are applicable to any potential. Variables are reduced with respect to the depth of the minimum in the potential,  $\epsilon$ , and its internuclear separation,  $r_m$ . The symbols  $K$ ,  $x$ ,  $L^*$ ,  $\phi(x)$ , and  $u(x, L^*)$  denote respectively the reduced energy, internuclear separation, orbital angular momentum, intermolecular potential, and effective potential. The capacity parameter

$$B = \frac{2\mu \epsilon r_m^2}{\hbar^2}, \text{ where } \mu \text{ denotes the reduced mass, and reduced}$$

angular momentum are related to the orbital angular momentum  $L$  by

$$L^2 = \hbar^2 B L^{*2} .$$

Figure 1 illustrates the effective potential for two values of  $L^*$  and defines some of the nomenclature employed for  $g = K - K_0 < 0$ . For  $g > 0$ , the turning point of the unbounded motion is denoted  $x_1$  and  $x_2 = x_3 = x_0$ . The parameters  $K_0$ ,  $x_0$ , and  $u'' = d^2u/dx^2|_{x_0, L^*}$  which characterize the nature of the relative maximum in  $u(x, L^*)$  are of course functions of  $L^*$  only:  $K_0$  always increases with  $L^*$ ;  $x_0$  decreases or remains constant; and  $u''$  exhibits a more complex dependence. The functional dependence of all three parameters on  $L^*$  is determined by the intermolecular potential; Figs. 2, 3, and 4 illustrate the dependence of  $K_0$ ,  $x_0$ , and  $u''$  on  $L^*$  for the Lennard-Jones (12 - 6) potential,

$$\phi(x) = x^{-12} - 2x^{-6} .$$

It is convenient to define a reduced external classical phase shift by

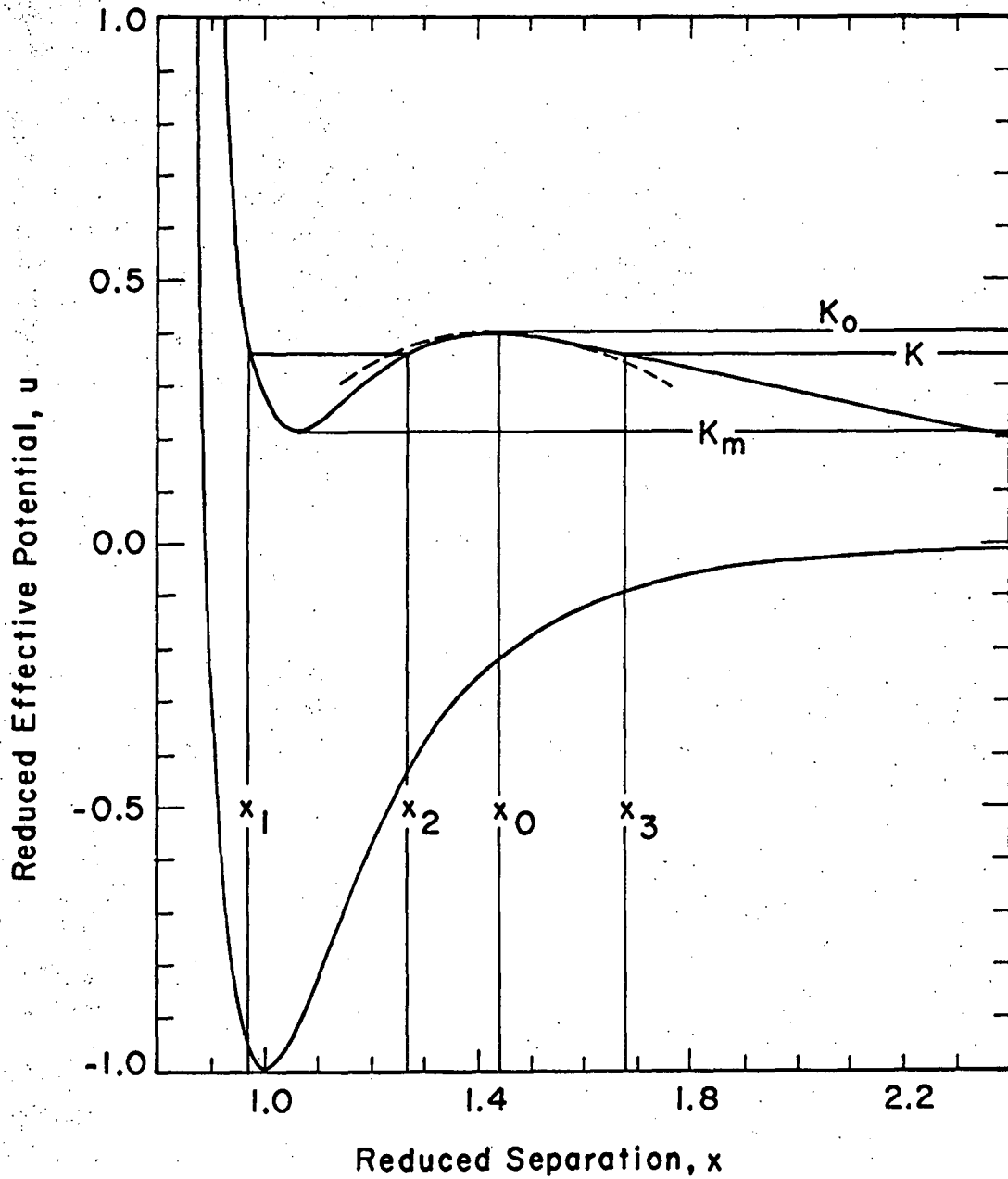
$$\delta_x^0(K, L^*) = \int_{x_3}^{\infty} [K-u]^{\frac{1}{2}} dx - \int_{L^*/K^{\frac{1}{2}}}^{\infty} [K-L^{*2}/x^2]^{\frac{1}{2}} dx, \quad (1a)$$

and a reduced internal classical phase integral by

$$I_2(K, L^*) = \int_{x_1}^{x_2} [K-u]^{\frac{1}{2}} dx . \quad (1b)$$

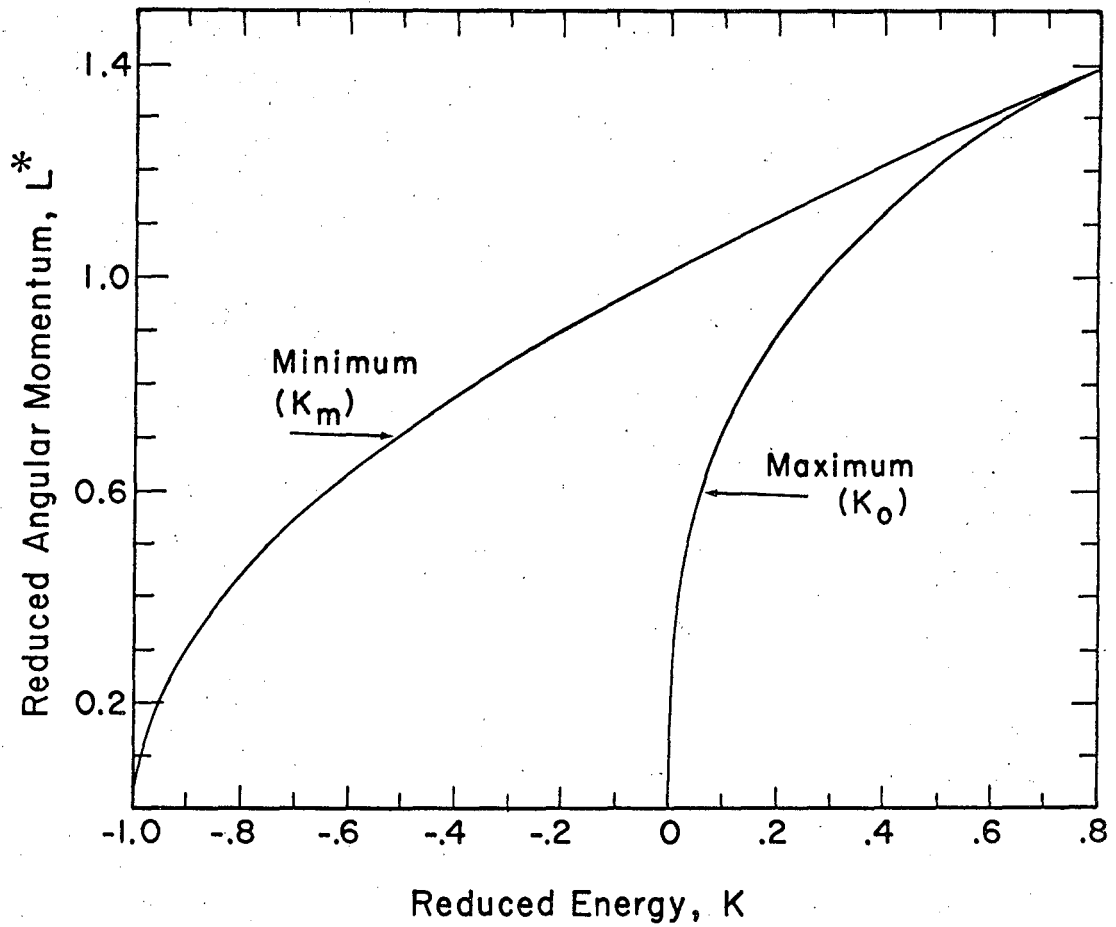
For values of  $x$  within a distance  $s$  of  $x_0$ , the effective potential may be expanded for a fixed value of  $L^*$  as





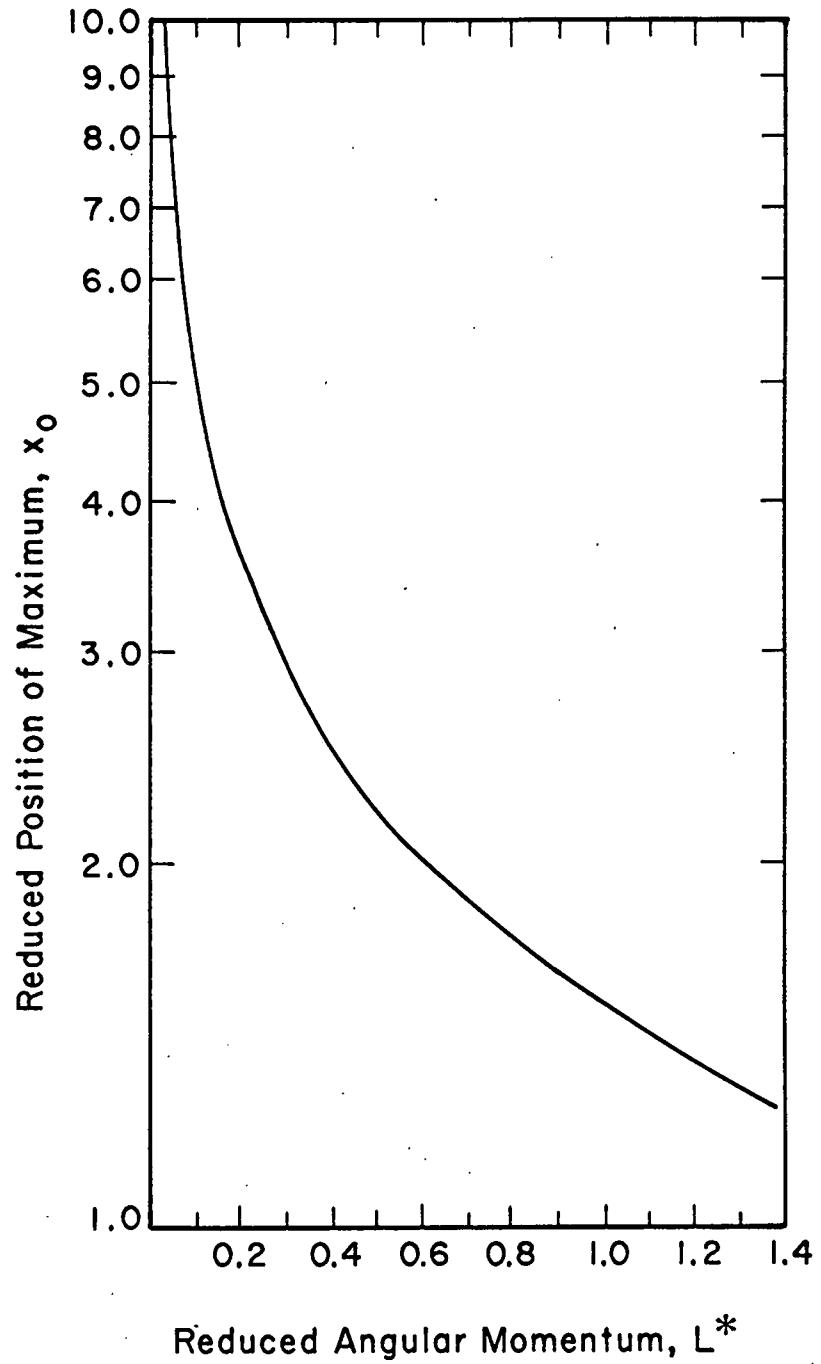
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Fig. 1. Plot of the reduced effective potential  $u = \phi + L^2/x^2$  versus  $x$  for  $L^* = 0.0$  (lower curve) and  $1.127$  (upper curve). The dashed curve is a parabolic fit to the maximum in the effective potential.



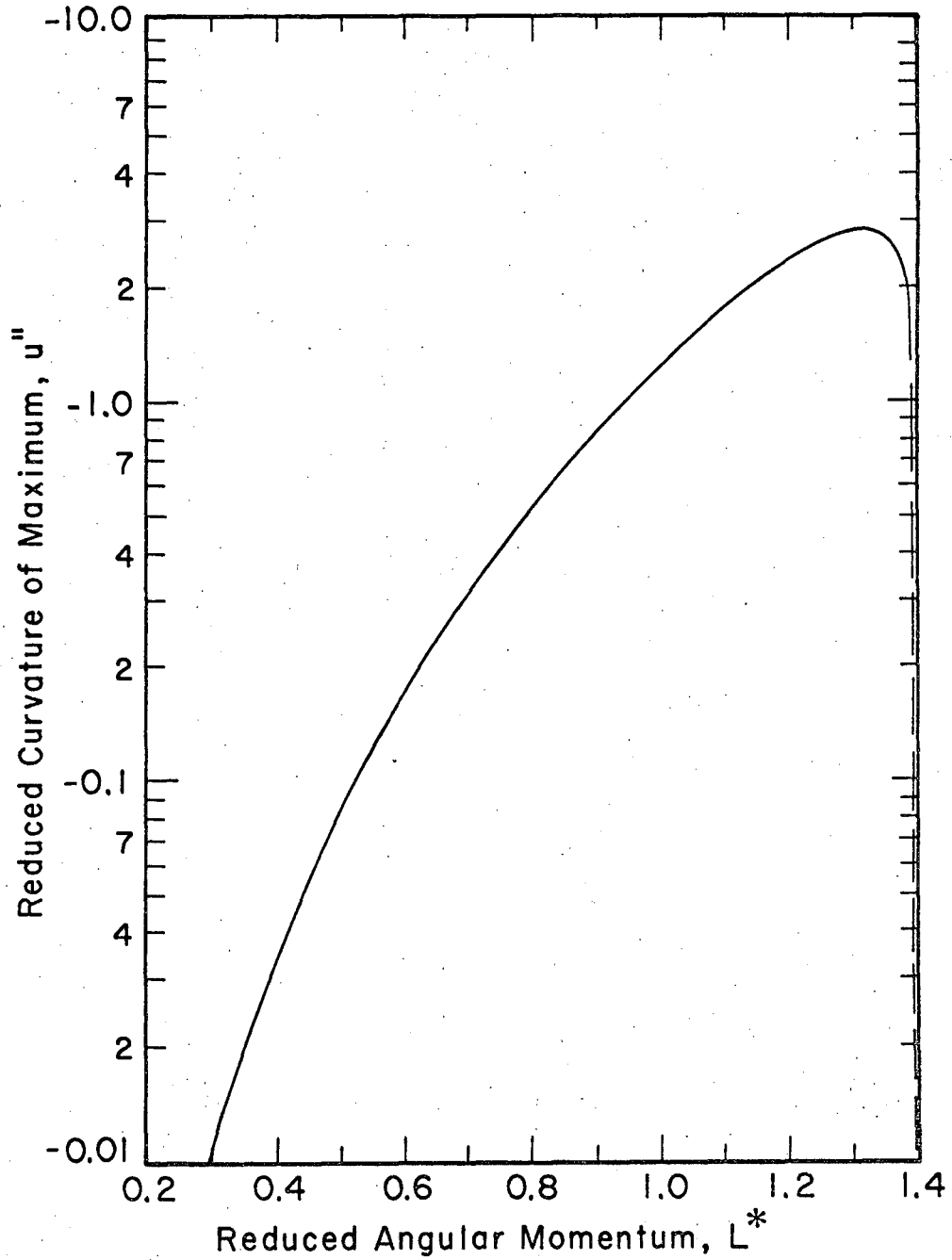
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Fig. 2. Plot of the energy of the maximum ( $K_o$ ) and the minimum ( $K_m$ ) in the effective potential vs.  $L^*$  for the Lennard-Jones (12-6) potential.



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Fig. 3. Plot of the reduced position of the maximum in the effective potential for the Lennard-Jones (12-6) potential.



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Fig. 4. Plot of the reduced curvature of the maximum in the effective potential vs.  $L^*$  for the Lennard-Jones (12-6) potential. The dashed line indicates that  $u''$  must climb rapidly and reach zero at the critical point where  $L^* = 1.397$ .

$$u(x, L^*) = K_0(L^*) + \frac{1}{2}u''(L^*)[x - x_0(L^*)]^2 + O(x - x_0)^3.$$

Consequently, the reduced phase integrals may be expressed, for small  $g$ , as:

$$\delta_x^0(K, L^*) = \int_{x_0+s}^{\infty} (K - u)^{\frac{1}{2}} dx - \int_{L^*/K^{\frac{1}{2}}}^{\infty} (K - L^{*2}/x^2)^{\frac{1}{2}} dx + F(s, K, L^*), \quad (2a)$$

$$I_2(K, L^*) = \int_{x_1}^{x_0-s} (K - u)^{\frac{1}{2}} dx + F(s, K, L^*), \quad (2b)$$

$$\text{and } F(s, K, L^*) = \left(-\frac{u''}{2}\right)^{\frac{1}{2}} \frac{s}{2} \sqrt{s^2 + |2g/u''|} + \frac{1}{2} \left(-\frac{2}{u''}\right)^{\frac{1}{2}} g \left\{ \ln(s + \sqrt{s^2 + |2g/u''|}) - \ln\left[\left(-\frac{2}{u''}\right)^{\frac{1}{2}} |g|^{\frac{1}{2}}\right] \right\}. \quad (2c)$$

These expressions for  $\delta_x^0$  and  $I_2$  will not depend on the particular choice of  $s$ , provided it is sufficiently small to ensure that the effective potential is adequately approximated by a parabola between  $x_0 - s$  and  $x_0 + s$ .

Expressions for the classical collision lifetime and deflection angle are now obtained by differentiating<sup>12</sup> Eqs. (2). Thus, the collision lifetime for  $g < 0$  is readily shown to be

$$\tau(K, L^*) = \tau_0 - \left(-\mu r_m^2/\epsilon u''\right)^{\frac{1}{2}} \ln |g|. \quad (3)$$

Eq. (3) was derived for a fixed value of  $L^*$ , and  $\tau_0$  and  $u''$  are functions of  $L^*$ ;  $\tau_0$  will depend on  $g$  as well, but the

energy dependence will be dominated for small  $g$  by the logarithmic singularity of the second term. A similar expression for  $g > 0$  is obtained with the nonsingular term  $\tau_0$  replaced by an analogous term  $\tau_1$  and with a slope to the logarithmic singularity of  $2(-\mu r_m^2/\epsilon u'')^{\frac{1}{2}}$ .

In a similar manner, the deflection angle may be derived from Eqs. (2) after first relating the energy separation variable  $g$ , which refers to fixed  $L^*$ , to the angular momentum displacement variable  $\rho = L^* - L_0^*$ , which refers to a fixed  $K$  such that  $K = K_0(L_0^*)$ . To first order in  $\rho$  the relation is

$$g = - 2L_0^* \rho/x_0^2 \quad (4)$$

and the deflection angle for fixed  $K$  and variable  $\rho$  is given by:

$$\chi = \chi_0 + \left( - \frac{2L_0^*}{x_0^4 u''} \right) \left[ 1 + (\rho/2u'') \frac{du''}{dL^*} \right] \ln \left| \frac{2}{u''} \frac{2L_0^*}{x_0^2} \rho \right|, \rho > 0 \quad (5a)$$

$$\chi = \chi_1 + 2 \left( - \frac{2L_0^*}{x_0^4 u''} \right)^{\frac{1}{2}} \left[ 1 + (\rho/2u'') \frac{du''}{dL^*} \right] \ln \left| \frac{2}{u''} \frac{2L_0^*}{x_0^2} \rho \right|, \rho < 0.$$

The variables  $\chi_0$  and  $\chi_1$  are nonsingular functions of  $K$  and  $\rho$ ;  $x_0$  is to be evaluated at  $L_0^*$ , but  $u''$  and  $du''/dL^*$  are functions of  $\rho$ . The singular behavior at very small  $\rho$  will be given by

$$\chi = \chi'_0 + a_0 \ln \rho, \quad \rho > 0 \quad (5b)$$

$$\chi = \chi'_1 + 2a_0 \ln |\rho|, \quad \rho < 0,$$

where  $\chi'_0$  and  $\chi'_1$  are regarded as constants and the slope  $a_0$

equals  $[-2L_0^*/x_0^4 u'']^{\frac{1}{2}}$ ; Eq. (5b) agrees with the expression derived by Eisberg and Porter.<sup>13</sup>

The expression for the classical lifetime, Eq. (3), is expected to have a wider range of validity than does the corresponding expression for the deflection angle, Eq. (5b), since Eq. (5a) is a more exact expression for finite  $\rho$  and the correspondence between  $g$  and  $\rho$  expressed in Eq. (4) is only approximate. Hirschfelder, et al.<sup>14</sup> have compiled a table of exact classical deflection angles for a Lennard-Jones (12 - 6) potential. Empirically, it is found that these exact values of  $\chi$  can be fit by Eq. (5b) over a range of  $|\rho| \sim 0.05$ . Generally, the slopes found empirically deviate from the predictions of Eq. (5b) by about 10 to 30%. The exact values do follow Eq. (5a) somewhat more closely, regarding  $\chi_0$  and  $\chi_1$  as constants: this is illustrated in Fig. 5 for  $K = 0.4$ .

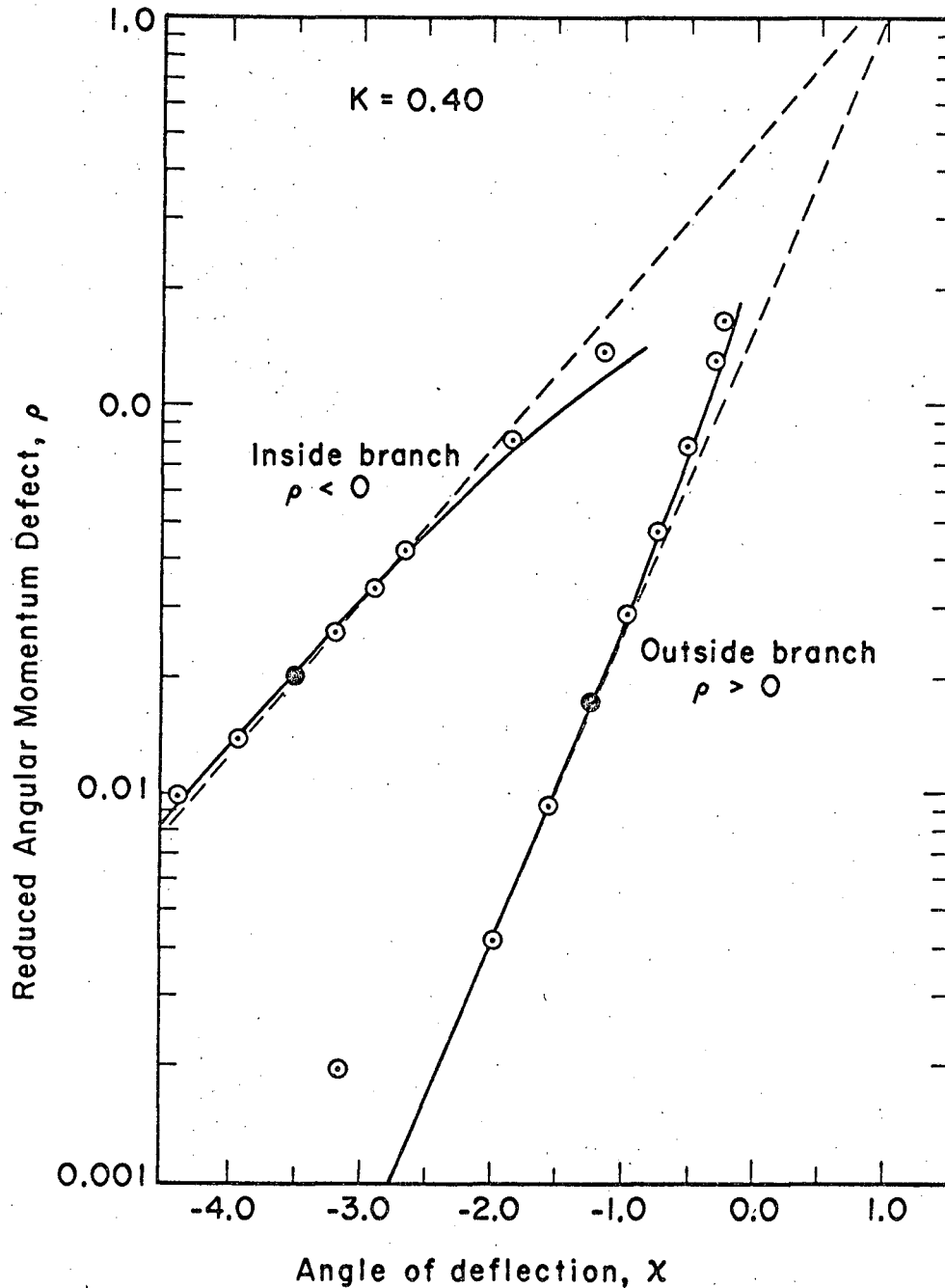


Fig. 5. The angle of deflection near an orbiting singularity vs. the reduced angular momentum defect  $\rho$ . The points are the exact values obtained by numerical integration given in Ref. 14 for the Lennard-Jones (12 - 6) potential. The dashed lines are obtained from Eq. (5b) ( $\chi'_0$  and  $\chi'_1$  regarded as constants). The solid curves are obtained from the more exact Eq. (5a) ( $\chi_0$  and  $\chi_1$  regarded as constants). The theoretical curves were fit to the exact points at  $\rho = -0.02$  and  $+0.0172$  (solid symbols) by adjusting  $\chi_0$ ,  $\chi'_0$ ,  $\chi_1$ , and  $\chi'_1$ .

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QUANTAL ORBITING

Ford, Hill, Wakano, and Wheeler<sup>11</sup> have derived a semi-classical expression for the phase shift applicable near a maximum in the effective potential which predicts the energy dependence of the phase shift for a fixed  $L_0^*$ . Schrödinger's equation was solved exactly for an inverted parabolic potential fitted to the maximum; this exact solution near the barrier maximum was joined onto JWKB solutions to the left and right of the barrier and the JWKB phases were developed to first power in the energy. By expanding the classical phase integrals of Eqs. (2) to first power in the energy displacement variable  $g$  and comparing with this more exact expression, it is possible to re-express the more exact expression<sup>15</sup> in terms of the classical integrals and an extended JWKB barrier penetration integral,

$$\theta = B^{\frac{1}{2}} I_3 = B^{\frac{1}{2}} \int_{x_2}^{x_3} [u - K]^{\frac{1}{2}} dx, \quad g < 0$$

$$\theta = -\pi w; \quad g > 0; \quad (6)$$

$w$  is the reduced energy displacement parameter employed in Ref. 14 and is related to  $g$  by

$$w = \left[ -\frac{B}{2u''} \right] g. \quad (7)$$

The resulting expression for the phase shift becomes:

$$\eta(K, L^*, B) = B^{\frac{1}{2}} \delta_x^0 - h(w) + t(w) + \tan^{-1} \left[ \frac{\exp(-\theta) \tan J}{\exp(-\theta) - 2 \tan J} \right] \quad (8a)$$

where the refined phase integral is defined as

$$J(K, L^*, B) = B^{\frac{1}{2}} I_2(K, L^*) - \pi/2 - h(w) + t(w). \quad (8b)$$

The correction formula  $h(w)$  and transition formula  $t(w)$  are defined as

$$h(w) = 0.5w \{ \ln[(w/e)^2 + (1/4\gamma)^2]^{\frac{1}{2}} - \ln(|w|/e) \}, \quad (9)$$

with  $\gamma = 1.78107$

and

$$t(w) = \frac{1}{2} \tan^{-1} e^{\pi w}, \quad (10)$$

and are plotted in Figs. 6 and 7 respectively.

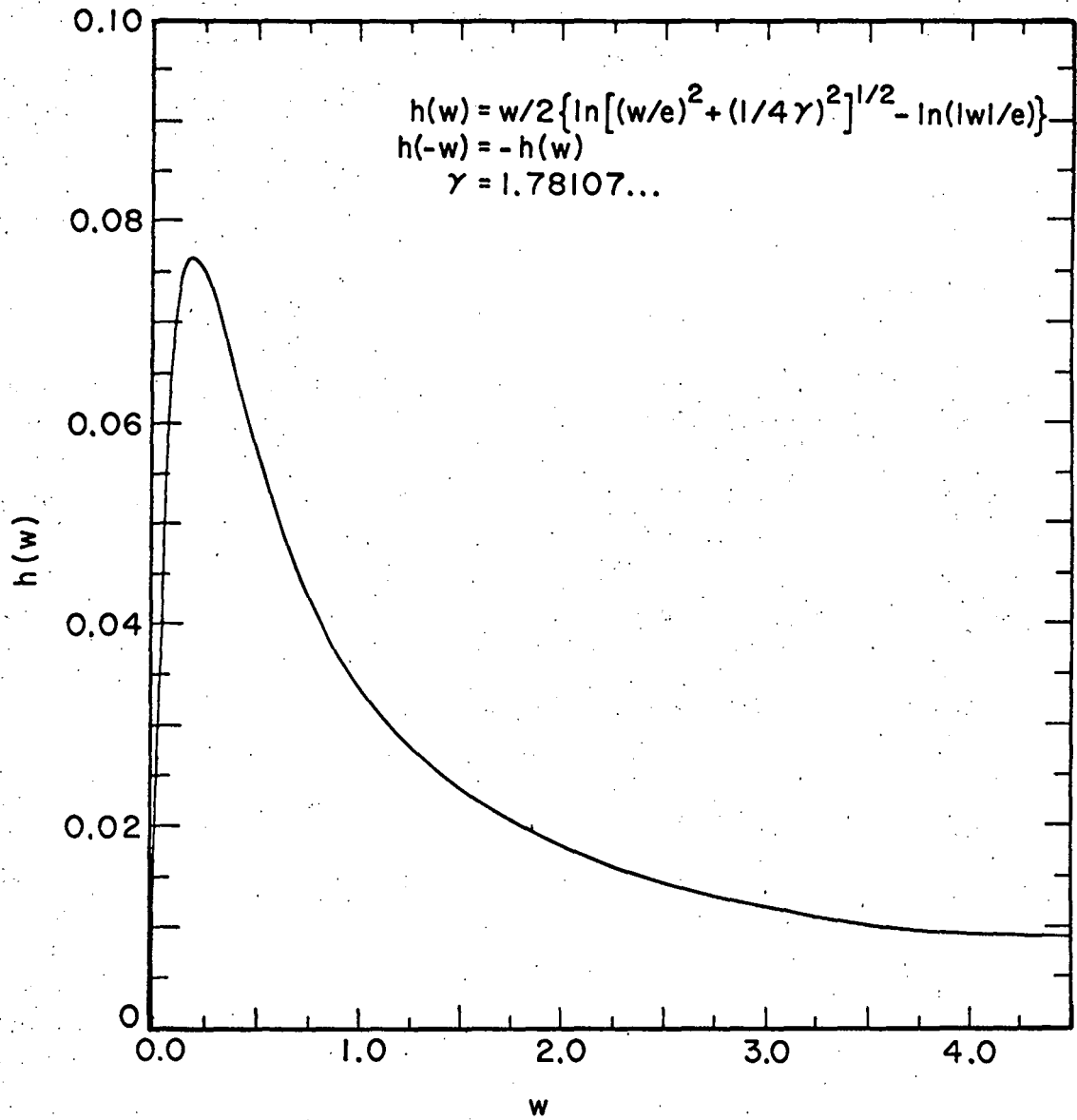
Qualitatively, Eq. (8a) exhibits the proper behavior for all energies. Thus, for  $g \gg 0$ , it simply reduces to the classical value,

$$\eta = B^{\frac{1}{2}} (\delta_x^0 + I_2).$$

The phenomena of tunnelling is also contained in Eq. (8a). Thus, for  $g \ll 0$ , the contribution from the internal phase is relatively constant, except when

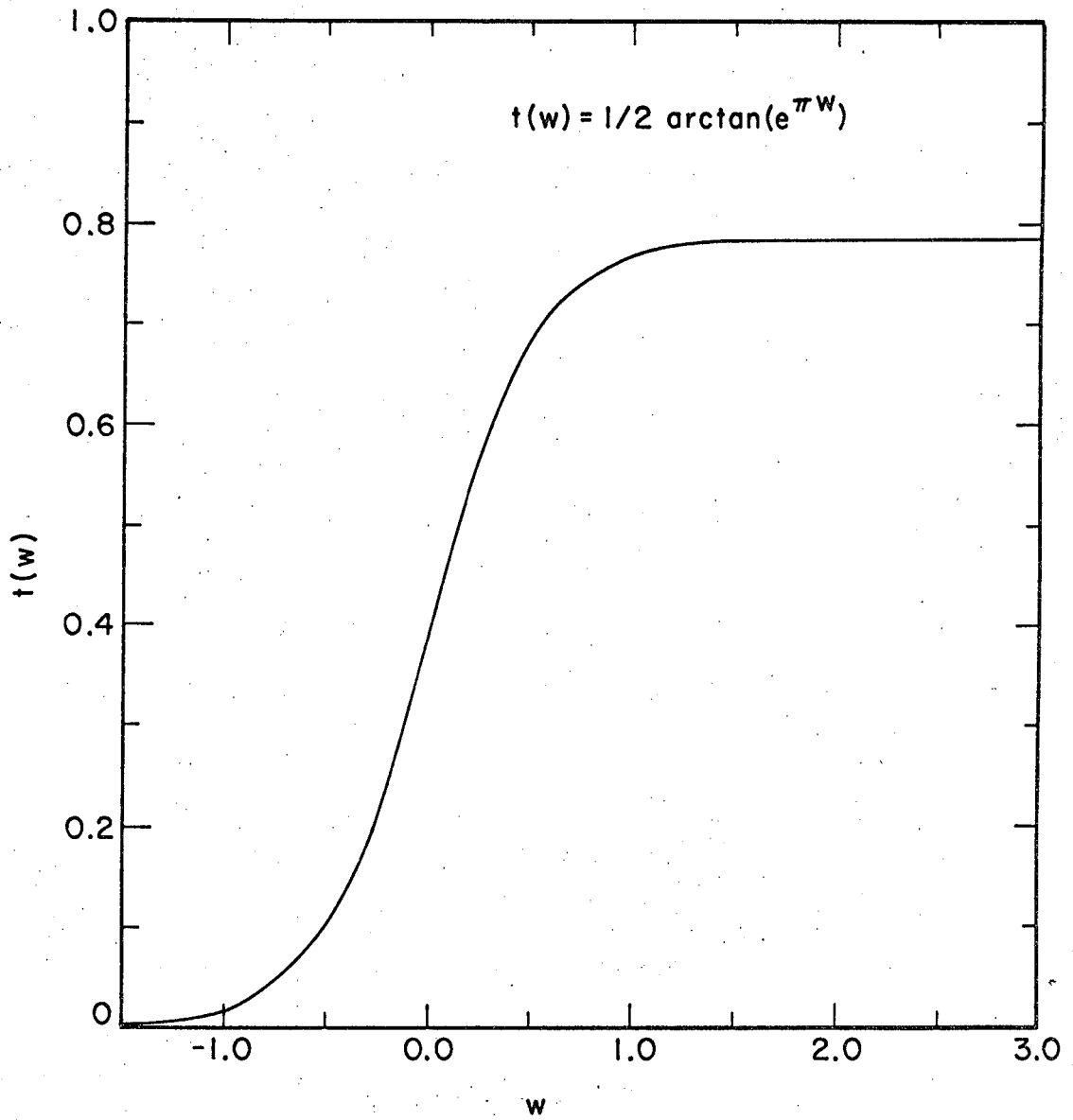
$$\tan J \sim 0.5 e^{-\theta}, \quad (11)$$

at which point an increment of  $\pi$  is quickly added to the phase shift. For  $g \sim 0$ , the increments of  $\pi$  from the internal phase are smoother and the infinite rate of change of the phase with  $g$  at  $g = 0$ , which is predicted by the classical expressions, Eq. (2), is removed through the correction



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Fig. 6. Plot of the quantal correction term  $h(w)$ , Eq. (9), versus  $w$ .



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Fig. 7. Plot of the transition term  $t(w)$ , Eq. (10), versus  $w$ .

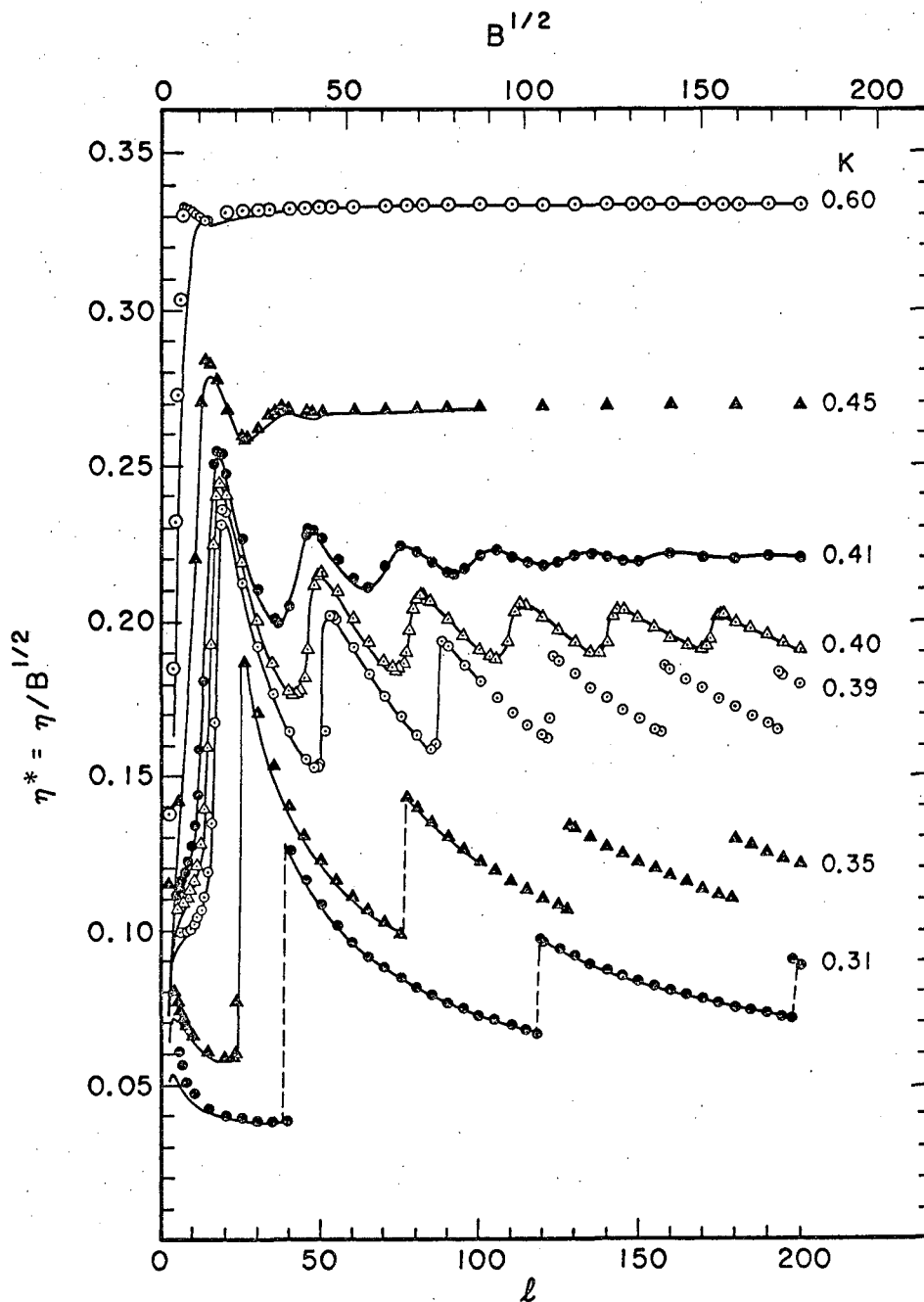
function  $h(w)$ . Recently, Curtiss and Powers<sup>16,17</sup> have obtained an expansion of the phase shift in powers of  $h$  which indicates that the phase shift in the classical limit for  $g < 0$ , where more than one turning point of the classical motion exist, is given by the phase integrals over all classically allowed regions. This behavior is also exhibited by Eq. (8a) since the contribution from the  $\tan^{-1}$  term is always with  $\pi$  of the value  $B^{\frac{1}{2}}I_2$ .

#### Comparison with Other Work

By means of Eqs. (4) and (8) the phase shift is readily calculated for any set of values of  $B$ ,  $K$ , and  $L^*$  from the graphs of  $K_0(L^*)$ ,  $x_0(L^*)$ ,  $u''(L^*)$ ,  $h(w)$ , and  $t(w)$  given in Figs. 2, 3, 4, 6, and 7 and the tables of the reduced integrals  $\delta_x^0(K, L^*)$ ,  $I_2(K, L^*)$ , and  $I_3(K, L^*)$  tabulated in the Appendix. Semiclassical phase shifts evaluated by this procedure are compared with published exact quantum mechanical calculations in Figs. 8 and 9. The semiclassical correspondence between  $L^*$  and the partial wave quantum numbers  $l$  was used,

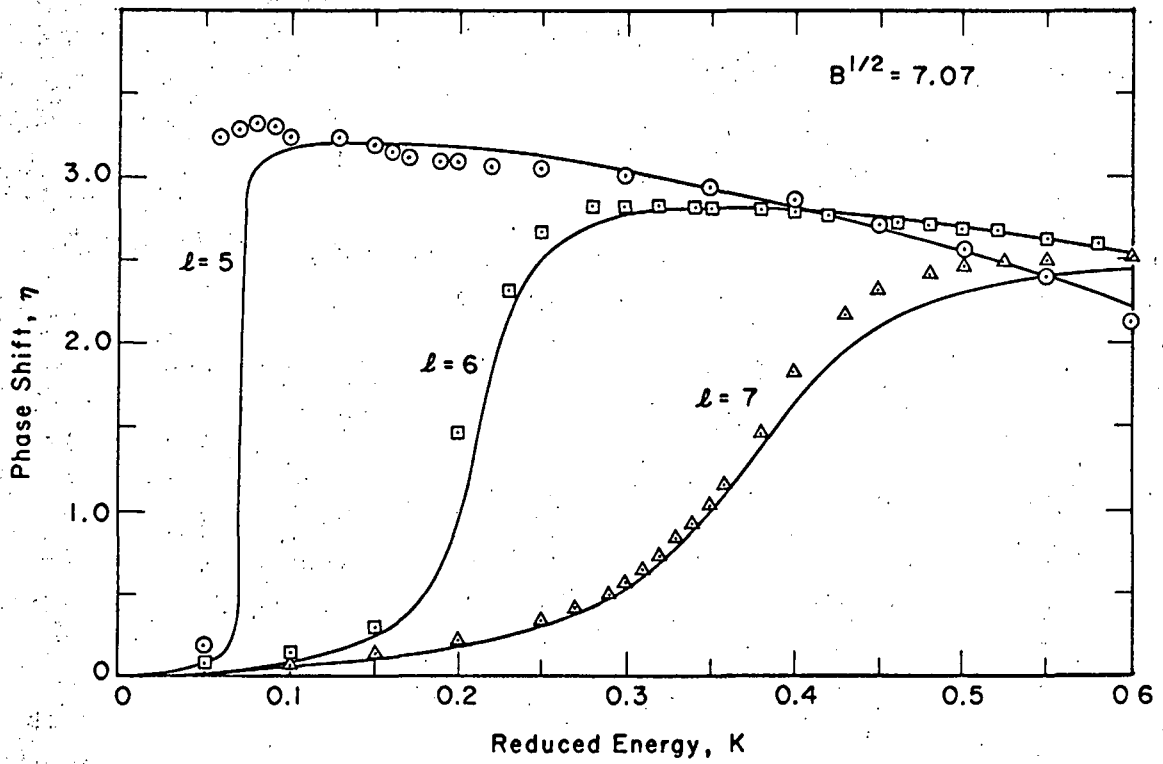
$$l + \frac{1}{2} = B^{\frac{1}{2}}L^*.$$

In general, the agreement is seen to be very good. The semiclassical expression tends to overestimate the phase shift at very small values of  $B$  ( $B^{\frac{1}{2}} \lesssim 5$ ). Expressions for correction terms to the semiclassical phase are known to become important at small values of  $B$ .<sup>9,19</sup> However, the range of validity of Eq. (8a),  $B^{\frac{1}{2}} \gtrsim 5$ , should include all atomic or molecular



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Fig. 8. Comparison of the exact quantum mechanical phase shifts of Ref. 7 (curves) with the semiclassical expression, Eq. (8a) (symbols). The calculations are for a Lennard-Jones (12-6) potential with  $L^* = 1.127$ ,  $K_0 = 0.4008$ .



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Fig. 9. Comparison of the exact quantum mechanical phase shifts of Ref. 6 (solid curves) with the semi-classical expression, Eq. (8a), for  $l = 5$  (circles), 6 (squares), and 7 (triangles).

scattering partners which are likely to be studied experimentally. Thus, even for the extreme case of H atoms scattering off a heavy target with  $\epsilon = 1$  kcal/mole and  $r_m = 2\text{\AA}$ ,  $B^{\frac{1}{2}}$  is about 9 and the semiclassical expression may be used with confidence for qualitative and good approximate quantitative predictions.

Recently, Livingston<sup>8</sup> has derived a semiclassical expression for the phase shift, by an eloquent application of phase integral methods, which is applicable to an attractive potential where classically three turning points exist; he has gone on to compare the predictions of this expression with the quantum calculations of Ref. 7. His expression is similar to the Ford, Hill, Wakano, and Wheeler expression<sup>11</sup> employed here. In fact, it is possible to directly compare the present work with Ref. 8, since Fig. 3 compares our results with those presented in Ref. 7. Numerical results presented in Ref. 8 for  $g < 0$  are in good agreement with those presented here ( $K = 0.31, 0.35, 0.39, 0.40$ ). Both semiclassical treatments reproduce the quantum calculations quite well for larger values of  $l$  and begin to fail for  $l \lesssim 10$ . The present results reproduce the undulations in the quantum calculations for  $g > 0$  as well; Ref. 8 predicts the qualitative structure for  $g > 0$ , but the extent of the quantitative agreement is not discussed. The resonances in the phase shift arise from paired virtual levels in Ref. 8, while the quantum calculations show no such pairing effect. However, the "center-of-gravity" of a pair



compares well with the position of the quantum resonance; moreover, the general shape of the quantum resonance is predicted semiquantitatively. In this connection, no detailed comparison with the shape of the resonances in the quantum calculations of Ref. 7 is presented here, and so it is not possible to directly compare with the results of Ref. 8 on this point. However, it should be pointed out that Eq. (8a) predicts no pairing of the resonance levels and is in this respect in better agreement with the quantum calculations. Finally, the equation derived in Ref. 8 predicts an infinite rate of change of  $\eta$  with  $K$  (or  $L^*$ ) at an orbiting singularity. In contrast, no such singularity in  $\partial\eta/\partial K$  is exhibited by the FHW equation employed here; as discussed later, this point could be of some importance to the computation of collision lifetimes.

#### Total Cross Sections

Qualitatively, the undulations in the phase shifts illustrated in Figs. 3 and 4 are expected to produce corresponding undulations in the total cross section. Sharp fluctuations in the total cross section for energies close to resonance with a metastable bound level are well known in nuclear scattering<sup>20</sup> and have also been discussed in treatments of atomic scattering.<sup>21,22</sup> The total cross section is readily evaluated from Eq. (8a) with the aid of the optical theorem. The results are most naturally expressed as

$$Q = Q_0 + \frac{4\pi r_m^2}{BK} \sum_{l_1}^{l_2} (2l+1) \left\{ \frac{e^{2\pi w \tan^2 J} \cos 2\eta_x + e^{\pi w \tan J} (e^{\pi w - 2 \tan J}) \sin \eta_x}{(e^{\pi w - 2 \tan J})^2 + e^{2\pi w \tan^2 J}} \right\} \quad (12)$$

where  $Q_0$  is given by

$$Q_0 = \frac{4\pi r_m^2}{BK} \text{Im} \left\{ i \sum_0^{l_1-1} (l+\frac{1}{2})(1-e^{2i\eta}) + \sum_{l_1}^{\infty} (l+\frac{1}{2})(1-e^{2i\eta_x}) \right\} .$$

The term  $\eta_x$  represents the external contribution to the phase shift and is given by the first three terms of Eq. (8a).

The partial wave  $l_2$  is chosen such that for  $l \geq l_2$  there exists only one turning point of the classical motion and  $\eta = \eta_x$  for all such  $l$ . The choice of  $l_1$  is dictated by the requirement that for  $l < l_1$  the phase shift be a smoothly varying function of  $l$ , i.e. that  $\eta(l)$  exhibit no undulations. Moreover, Eq. (12) is strictly valid only for small values of  $g$ ; for barrier maxima  $K_0$  much greater than  $K$ , the factor  $\pi w$  should be replaced everywhere it appears in the argument of an exponential function by the negative of the barrier penetration integral,  $-\theta$ .

The dependence of  $Q_0$  on  $K$  is expected to be smooth; it should decrease monotonically with increasing  $K$ , with possible rather smooth glory undulations<sup>1</sup> superimposed on this monotonic decrease. In contrast, the second and third terms in Eq. (12) are expected to lead to sharp fluctuations in the dependence of  $Q$  on  $K$ , arising from partial waves which satisfy the resonance condition expressed in Eq. (11). The qualitative

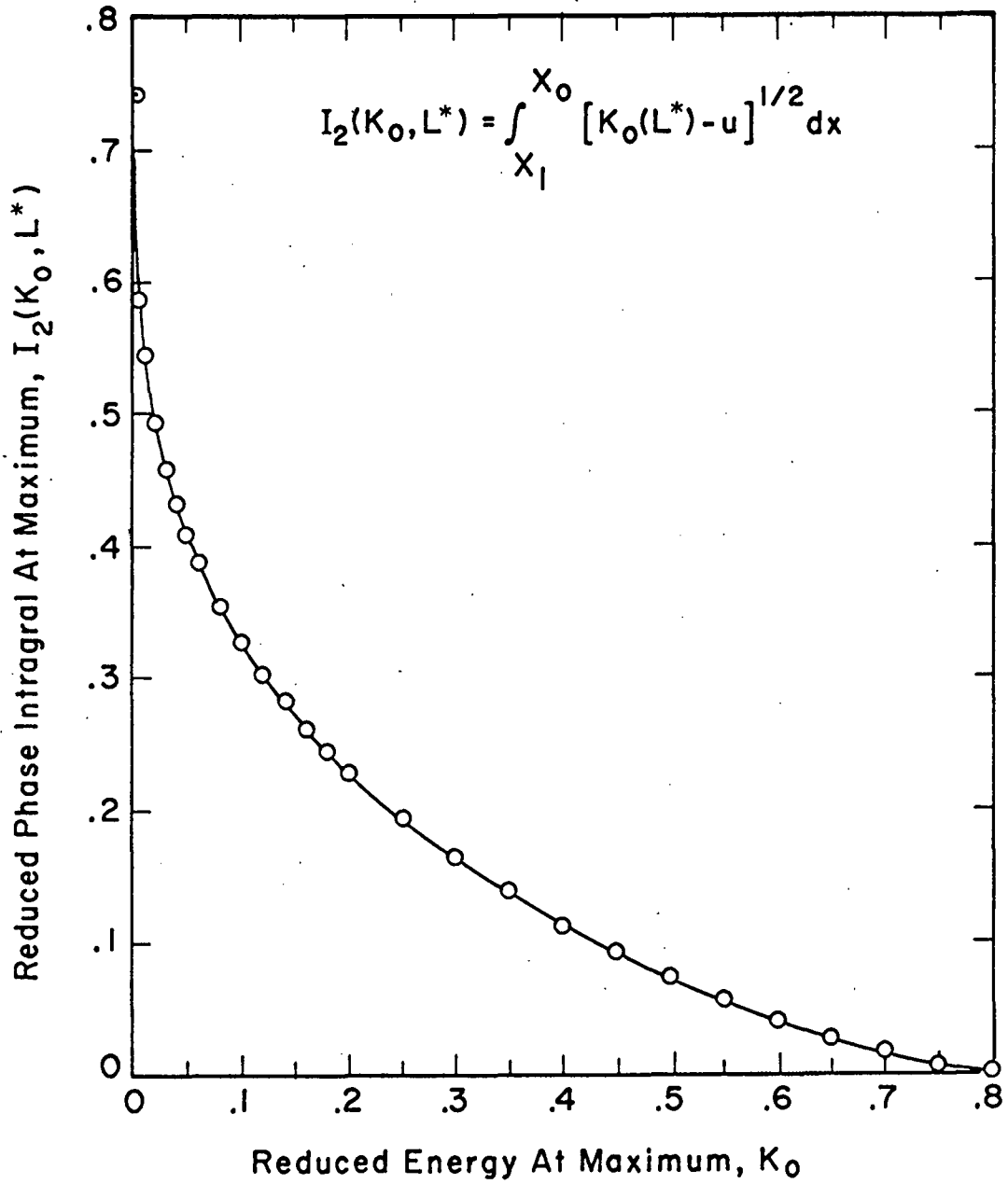
origin of these resonances in  $Q(K)$  is illustrated by Eq. (12). For  $g < 0$ , the ambient rather smooth contribution of the  $l$ th partial wave to  $Q$  is given by  $(4\pi r_M^2/BK) (2l + 1) \sin^2 \eta_x$ . If  $\eta_x$  is near zero or a multiple of  $\pi$ , this contribution will be small. In this case, only the first resonant term of Eq. (12) will contribute appreciably and will result in a positive spike in  $Q$ , since  $\cos 2\eta_x \sim 1$ . This is exactly the behavior expected qualitatively. In a similar manner, for  $\eta_x \sim \pi/2, 3\pi/2, \text{ etc.}$ , the ambient external contribution will be a maximum and a large negative spike in  $Q$  will appear at resonance. For  $\eta_x \sim \pi/4, 3\pi/4, 5\pi/4, \text{ etc.}$ ,  $\sin^2 \eta_x \sim \frac{1}{2}$  and a sudden increment of  $\pi$  in the phase shift should lead to sharp positive and negative spikes in  $Q$ . Once again, this behavior is exhibited by Eq. (12), as now the second resonant term is dominant.

The breadth of these spikes in the total cross section will decrease very rapidly as  $w$  becomes more negative due to the exponential dependence on the barrier penetration integral expressed in Eq. (12). Thus, for  $w \lesssim -1$ , these sudden spikes will probably prove experimentally unobservable, since the measured cross section is necessarily an average over the experimental band pass of the velocity selector employed. On the other hand, for  $w \gtrsim 1$ , the width of these resonances will become very broad and merge into a colorless spectrum. Consequently, observable resonances in  $Q$  are expected when the resonance condition is satisfied for  $w \sim 0$ , i.e. when  $J(K_0(l), l) \sim 0.46$  or

$$I_2(K_0(L^*), L^*) = B^{-\frac{1}{2}} (1.64 + n\pi). \quad (13)$$

It is difficult to see how to formulate a more exact requirement for the expected location of the resonance contributions to  $Q$ . For  $w \sim 0$ , the considerations of the last paragraph are not helpful because  $\eta_x$  is a rapidly varying function of  $K$  due to large contributions from the  $t(w)$  term. Thus, the exact resonant energies can be predicted only by a numerical analysis for each case based on Eq. (12) because of the simultaneous rapid variation in  $e^{\pi w}$ ,  $J$ , and  $\eta_x$ . Nevertheless, Eq. (13) may be used to locate the approximate resonance energies. The absolute value of  $w$  is expected to be less than unity at an observable resonance and this establishes a maximum uncertainty in the resonant energy of  $\pm (-2u''/B)^{\frac{1}{2}}$ .

The observable resonant energies for any capacity parameter  $B$  are readily estimated from Eq. (13) and the reduced internal phase integral at maximum plotted in Fig. 10. Values for resonance energies for H scattering off of Hg, where  $B^{\frac{1}{2}}$  is expected to be 25.9,<sup>23</sup> evaluated in this manner differ from the more accurate values deduced in Ref. 22 (the present analysis predicts 0.53, 0.27, 0.12, 0.04, 0.007, whereas Ref. 22 predicts 0.60, 0.26, 0.08, 0.02, and 0.003); this reflects the fact that a Lennard-Jones (12-6) potential is a poor description of the HgH molecule. Indeed, experimental observation of resonances in hydrogen scattering studies together with isotopic substitution may prove to be a sensitive method of investigating the shape as well as the range of the intermolecular potential.



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Fig. 10. Plot of the reduced internal phase integral at maximum versus  $K_0$ .

### Differential Cross Section

The nature of the classical differential cross section near an orbiting singularity and a qualitative description of the quantal corrections expected is given in Ref. 2. We wish to emphasize the point made in Ref. 2 that the role of the correction function  $h(w)$  in Eqs. (8) is to remove the infinite rate of change of  $\delta_x^0$  and  $I_2$  with  $L^*$  predicted classically, which leads to the classical singularity in the deflection function expressed in Eqs. (5b).

In analogy to the case of the total cross section, resonance effects will not be observable in the differential cross section unless  $|w| < 1$ . Consequently, the number of partial waves where quantal corrections due to the barrier maxima are expected is readily estimated to be

$$\Delta l \sim a_0^{-1}$$

where  $a_0$  is the slope parameter in the classical deflection function, Eq. (5b). For a Lennard-Jones (12-6) potential,  $a_0$  varies very little for values of  $K$  between 0.1 and 0.6 and is about 0.5. Consequently, in analyzing the differential cross section near orbiting, it will be necessary to evaluate explicitly the contribution from only two or three partial waves: the contributions from other partial waves may be evaluated by standard semiclassical techniques.<sup>2</sup>

For scattering of H atoms, two or three partial waves correspond to a spread in  $L^*$  of about 0.1. Fig. 5 illustrates that this is typically the range of validity of Eqs. (5b). Consequently, the exponential decrease with increasing angle

expected<sup>2</sup> in the classical differential cross section for a deflection function satisfying Eqs. (5b) will be destroyed and the wide angle scattering of H atoms should be entirely quantal. In contrast, scattering of heavier atoms, for which  $B^{\frac{1}{2}} \gtrsim 200$ , should be described by the classical equations (with possible semiclassical interference between the two branches).<sup>2,1</sup> In particular, in the chemical reactions of alkali metals with halogens, it has been proposed that all trajectories which pass over the rotational barrier react while the others scatter elastically.<sup>24</sup> In these collisions  $B^{\frac{1}{2}}$  is very large, quantal corrections should be negligible (except possibly at  $\chi = \pi$ ), and only contributions from  $\rho > 0$  contribute to the elastic scattering so that the wide angle elastic scattering should exhibit the expected exponential fall-off to the extent that Eqs. (5b) rather than (5a) adequately approximate  $\chi(L^*)$ .

#### Lifetimes

The lifetime or duration of a collision,  $\tau$ , has been defined quantum mechanically and is obtained from the derivative of the phase shift with respect to energy.<sup>25</sup> We limit ourselves in this section to pointing out that the "quantal" or improved semiclassical expression for  $\tau$ , obtained by differentiating Eq. (8a), does not exhibit the divergence expressed in the simple classical result, Eq. (3); this divergence is exactly cancelled by the correction function  $h(w)$  which appears in Eqs. (8). Thus, differentiation of Eq. (8a) leads to phase shifts with the correct quantal features, i.e.,  $\tau$  is finite for

all  $K$  and  $L^*$  and  $\tau$  will exhibit sharp fluctuations (resonances) when the incident energies pass through values for which the resonance condition expressed in Eq. (11) is satisfied. Consequently, expressions for three-body kinetic recombination rates<sup>26</sup> and the thermodynamics of real gases<sup>27</sup> which have been formulated in terms of the distribution in collision lifetimes may be handled within the framework of a classical theory by employing Eq. (8a) to incorporate the quantal corrections.

#### ACKNOWLEDGEMENTS

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APPENDIX

REDUCED PHASE INTEGRALS FOR A LENNARD-JONES (12-6)  
POTENTIAL

Tables of the reduced phase integrals  $\delta_x^0(K, L^*)$  and  $I_2(K, L^*)$  and of the barrier penetration integral  $I_3(K, L^*)$  for a Lennard-Jones (12-6) potential were prepared by numerical integration of Eqs. (1b) and (6) using 500 subintervals. The effect of varying the integration step size was investigated for random values of  $K$  and  $L^*$ . Thus, values of  $I_2(0.2, 1.0)$  and  $I_3(0.2, 1.0)$  computed with 500 subintervals were within 0.01% of values computed with 1000, 5000, and 10,000 subintervals.

The external phase shift was evaluated by expressing Eq. (1a) as

$$\delta_x^0(K, L^*) = \int_{x_3}^{\infty} \left\{ (K - u(x, L^*))^{\frac{1}{2}} - (K - L^{*2}/x^2)^{\frac{1}{2}} \right\} dx \\ + L^* \cos^{-1} (L^*/K^{\frac{1}{2}}x_3) - (Kx_3^2 - L^{*2})^{\frac{1}{2}}$$

where it is understood that the  $\cos^{-1}$  of a number greater than unity and the square root of negative numbers are both taken as zero. In practice, the upper limit of the integration was taken as 20 rather than infinity. For most of the entries in the Table, this results in negligible error; in the most extreme entry,  $K = 0.05$  and  $L^* = 1.50$ , it results in less than 1% error. The integration was performed by dividing the interval from  $x_3$  to 20 into 5000 subintervals. Variation of the number of intervals from 2000 to 8000 indicated that the entries in Table I for high values of  $L^*$  where  $\delta_x^0$  is relatively

small may be in error by about 1%. Furthermore, at high values of  $L^*$ ,  $\delta_x^0$  should converge to the value predicted by the first Born approximation,

$$\delta_x^0 \text{ (Born)} = (3\pi K^2/16L^{*5});$$

this behavior is indeed found. Entries in the Table for high values of  $L^*$  are within a few percent of the Born approximation.

REDUCED EXTERNAL PHASE INTEGRAL

Values of K

---

L*	0.050000	0.100000	0.150000	0.200000	0.250000
0.05	-1.487291	-2.135351	-2.632697	-3.052002	-3.421429
0.10	-0.953822	-1.410988	-1.762185	-2.058393	-2.319423
0.15	-0.679626	-1.050492	-1.336179	-1.577398	-1.790095
0.20	-0.492343	-0.809429	-1.055038	-1.262867	-1.446337
0.25	-0.349270	-0.626745	-0.843741	-1.028038	-1.191056
0.30	-0.234466	-0.479202	-0.673590	-0.839642	-0.986971
0.35	-0.140882	-0.355972	-0.531061	-0.681931	-0.816391
0.40	-0.065365	-0.251430	-0.408963	-0.546454	-0.669780
0.45	-0.006737	-0.161982	-0.302480	-0.427462	-0.540600
0.50	0.033190	-0.086702	-0.209968	-0.322851	-0.426385
0.55	0.048247	-0.025136	-0.130087	-0.230797	-0.324951
0.60	0.024026	0.022117	-0.062255	-0.150235	-0.234919
0.65	0.014428	0.052706	-0.006828	-0.081014	-0.155889
0.70	0.009450	0.059879	0.035929	-0.022332	-0.086542
0.75	0.006513	0.032126	0.0633494	0.024825	-0.027384
0.80	0.004639	0.020920	0.0691193	0.059095	0.021199
0.85	0.003393	0.014640	0.039625	0.077274	0.057906
0.90	0.002533	0.010670	0.026662	0.063232	0.080704
0.95	0.001932	0.007979	0.019221	0.038781	0.082152
1.00	0.001487	0.006089	0.014375	0.027625	0.049666
1.05	0.001158	0.004743	0.011019	0.020637	0.034949
1.10	0.000922	0.003725	0.008601	0.015863	0.026150
1.15	0.000731	0.002966	0.006815	0.012432	0.020194
1.20	0.000594	0.002394	0.005470	0.009930	0.015927
1.25	0.000484	0.001937	0.004420	0.007997	0.012750
1.30	0.000399	0.001596	0.003628	0.006498	0.010349
1.35	0.000330	0.001317	0.002991	0.005370	0.008482
1.40	0.000279	0.001102	0.002489	0.004473	
1.45	0.000233	0.000927	0.002091	0.003726	
1.50	0.000189	0.000778	0.001778	0.003131	

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REDUCED EXTERNAL PHASE INTEGRAL (Cont'd.)

Values of K

---

L*	0.300000	0.350000	0.400000	0.450000	0.500000
0.05	-3.755423	-4.062567	-4.348452	-4.616963	-4.870928
0.10	-2.555448	-2.772520	-2.974581	-3.164372	-3.343890
0.15	-1.982490	-2.159480	-2.324263	-2.479061	-2.625497
0.20	-1.612417	-1.765276	-1.907644	-2.041424	-2.168004
0.25	-1.338804	-1.474906	-1.601745	-1.720988	-1.833856
0.30	-1.120752	-1.244147	-1.359252	-1.467541	-1.570098
0.35	-0.938824	-1.051963	-1.157642	-1.257164	-1.351493
0.40	-0.782512	-0.886956	-0.984696	-1.076871	-1.164331
0.45	-0.644579	-0.741257	-0.831959	-0.917658	-0.999094
0.50	-0.522250	-0.611819	-0.696136	-0.776003	-0.852043
0.55	-0.413046	-0.495900	-0.574250	-0.648713	-0.719787
0.60	-0.315345	-0.391675	-0.464300	-0.533624	-0.600012
0.65	-0.228583	-0.298458	-0.365494	-0.429859	-0.491765
0.70	-0.151089	-0.214302	-0.275657	-0.335037	-0.392480
0.75	-0.083151	-0.139369	-0.194865	-0.249174	-0.302125
0.80	-0.024735	-0.073381	-0.122675	-0.171700	-0.220028
0.85	0.023607	-0.016570	-0.059127	-0.102527	-0.146004
0.90	0.060710	0.030550	-0.004440	-0.041689	-0.079959
0.95	0.084837	0.066843	0.040782	0.010493	-0.022036
1.00	0.090064	0.090438	0.075277	0.053247	0.027279
1.05	0.058211	0.095853	0.097193	0.085358	0.067112
1.10	0.040790	0.063815	0.100454	0.104487	0.096191
1.15	0.030665	0.045000	0.066461	0.103401	0.111464
1.20	0.023803	0.034087	0.047565	0.066810	0.103147
1.25	0.018917	0.026613	0.036415	0.048894	0.065673
1.30	0.015217	0.021259	0.028672	0.037800	0.049141
1.35	0.012436	0.017245	0.023080	0.030072	0.038500
1.40	0.010268	0.014167	0.018880	0.024380	0.030901
1.45	0.008545	0.011763	0.015586	0.020041	0.025253
1.50	0.007147	0.009837	0.013005	0.016679	0.020886

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REDUCED EXTERNAL PHASE INTEGRAL (Cont'd.)

Values of K

---

L*	0.550000	0.600000
0.05	-5.112483	-5.343287
0.10	-3.514641	-3.677797
0.15	-2.764794	-2.897905
0.20	-2.288436	-2.403536
0.25	-1.941272	-2.043959
0.30	-1.667745	-1.761127
0.35	-1.441365	-1.527356
0.40	-1.247731	-1.327587
0.45	-1.076840	-1.151353
0.50	-0.924750	-0.994521
0.55	-0.787881	-0.853331
0.60	-0.663782	-0.725202
0.65	-0.551428	-0.609046
0.70	-0.448084	-0.501968
0.75	-0.353681	-0.403867
0.80	-0.267458	-0.313807
0.85	-0.189154	-0.231762
0.90	-0.118579	-0.157164
0.95	-0.055749	-0.090037
1.00	-0.000975	-0.030566
1.05	0.045228	0.020931
1.10	0.081704	0.063646
1.15	0.107169	0.096545
1.20	0.117324	0.117487
1.25	0.092992	0.120768
1.30	0.063715	0.084147
1.35	0.048665	0.061166
1.40	0.038546	0.047622
1.45	0.031242	0.038187
1.50	0.025792	0.031239

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## REDUCED INTERNAL PHASE INTEGRAL

Values of K

L*	0.050000	0.100000	0.150000	0.200000	0.250000
0.05	1.777593	2.288381	2.689304	3.031773	3.336248
0.10	1.310392	1.632956	1.889031	2.109228	2.305889
0.15	1.094113	1.334907	1.527664	1.694255	1.843570
0.20	0.956153	1.149683	1.305488	1.440653	1.562137
0.25	0.853415	1.016048	1.147364	1.261574	1.364432
0.30	0.769402	0.910514	1.024433	1.123631	1.213080
0.35	0.696226	0.821910	0.922959	1.010922	1.090271
0.40	0.629481	0.744149	0.835474	0.914800	0.986317
0.45	0.565932	0.673005	0.756799	0.829267	0.894490
0.50	0.503475	0.606659	0.684814	0.751899	0.812089
0.55	0.437908	0.543334	0.617544	0.680462	0.736627
0.57	0.404735				
0.58	0.389706				
0.59	0.377077				
0.60	0.365486	0.481477	0.553514	0.613351	0.666348
0.62	0.343921				
0.65	0.314319	0.419380	0.491767	0.549687	0.600359
0.67	0.295688				
0.70	0.268882	0.352282	0.430444	0.487632	0.536683
0.72	0.251588	0.317523			
0.73	0.243077	0.303164			
0.74	0.234647	0.290418			
0.75	0.226308	0.278558	0.368220	0.426606	0.474915
0.77	0.209815	0.256532			
0.80	0.185515	0.226112	0.300999	0.365332	0.414090
0.82	0.169563	0.206993	0.266157		
0.83	0.161651	0.197683	0.250703		
0.84	0.153782	0.188518	0.237327		
0.85	0.145948	0.179486	0.224994	0.301798	0.353262
0.87	0.130388	0.161758	0.202214		
0.90	0.107283	0.135876	0.170917		0.290848
0.91	0.099643	0.127414	0.160999	0.209171	
0.92	0.092025	0.119017	0.151276	0.195346	
0.93	0.084433	0.110687	0.141746	0.182712	
0.94	0.076865	0.102416	0.132365	0.170800	
0.95	0.069321	0.094208	0.123125	0.159417	0.222584
0.97	0.054295	0.077942	0.105009	0.137826	0.186754
0.98	0.046815	0.069882	0.096111	0.127479	0.170927
0.99	0.039353	0.061869	0.087316	0.117379	0.157189
1.00	0.031908	0.053896	0.078606	0.107485	0.144496

REDUCED INTERNAL PHASE INTEGRAL, Cont'd.

Values of K

---

L*	0.050000	0.100000	0.150000	0.200000	0.250000
1.01	0.024480	0.045964	0.069979	0.097780	0.132517
1.02	0.017076	0.038070	0.061420	0.088231	0.121054
1.03	0.009685	0.030211	0.052943	0.078842	0.110000
1.04	0.002310	0.022388	0.044529	0.069577	0.099281
1.05		0.014599	0.036178	0.060435	0.088843
1.06		0.006840	0.027883	0.051403	0.078646
1.07			0.019646	0.042470	0.068660
1.08			0.011459	0.033632	0.058861
1.09			0.003320	0.024879	0.049226
1.10				0.016211	0.039736
1.11				0.007612	0.030383
1.12					0.021152

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REDUCED INTERNAL PHASE INTEGRAL (Cont'd.)

Values of K

L*	0.300000	0.350000	0.400000	0.450000	0.500000
0.05	3.613403	3.869661	4.109244	4.335115	4.549441
0.10	2.485523	2.652068	2.808124	2.955526	3.095620
0.15	1.980326	2.107391	2.226666	2.339495	2.446869
0.20	1.673644	1.777428	1.874990	1.967394	2.055424
0.25	1.458996	1.547130	1.630076	1.708714	1.783696
0.30	1.295407	1.372212	1.444556	1.513196	1.578687
0.35	1.163343	1.231551	1.295834	1.356855	1.415106
0.40	1.052171	1.113651	1.171604	1.226630	1.279172
0.45	0.945050	1.010513	1.063301	1.113424	1.161286
0.50	0.867380	0.918935	0.967501	1.013599	1.057609
0.55	0.788084	0.835987	0.881067	0.923826	0.964628
0.60	0.714705	0.759611	0.801803	0.841776	0.879888
0.65	0.646312	0.688830	0.728680	0.766371	0.802262
0.70	0.580762	0.621332	0.659227	0.694985	0.728975
0.75	0.517716	0.556810	0.593152	0.627330	0.659740
0.80	0.456280	0.494373	0.529538	0.562457	0.593570
0.85	0.395749	0.433395	0.467792	0.499781	0.529877
0.90	0.335198	0.373154	0.407269	0.438685	0.468050
0.95	0.273239	0.312791	0.347294	0.378578	0.407537
1.00	0.206553	0.251004	0.287072	0.318866	0.347840
1.03	0.155255				
1.04	0.139487				
1.05	0.125655	0.184581	0.225205	0.258660	0.288286
1.08	0.089190	0.134125			
1.09	0.078026	0.116992			
1.10	0.067199	0.102581	0.158263	0.196525	0.228037
1.13	0.036273	0.065162	0.106156		
1.14	0.026374	0.053767	0.089839		
1.15	0.016643	0.042737	0.075632	0.128121	0.165280
1.16	0.007063	0.032008	0.062515		
1.17		0.021536	0.050122		
1.18		0.011289	0.038273	0.074135	
1.19			0.026860	0.059219	
1.20			0.015789	0.045627	0.093807
1.21			0.005024	0.032866	
1.22				0.020733	0.055254
1.23				0.009062	0.040150
1.24					0.026404
1.25					0.013518



REDUCED INTERNAL PHASE INTEGRAL (Cont'd.)

Values of K

---

L*	0.550000	0.600000
0.05	4.753870	4.949688
0.10	3.229435	3.357772
0.15	2.549547	2.648120
0.20	2.139684	2.220641
0.25	1.855519	1.924576
0.30	1.641459	1.701845
0.35	1.470962	1.524717
0.40	1.329567	1.378079
0.45	1.207196	1.251395
0.50	1.099819	1.140454
0.55	1.003749	1.041399
0.60	0.916407	0.951537
0.65	0.836619	0.869647
0.70	0.761470	0.792673
0.75	0.690667	0.720323
0.80	0.623185	0.651528
0.85	0.558426	0.585679
0.90	0.495776	0.522148
0.95	0.434697	0.460405
1.00	0.374745	0.400032
1.05	0.315349	0.340512
1.10	0.255934	0.281408
1.15	0.195413	0.221937
1.20	0.131636	0.160982
1.25	0.050684	0.095366
1.26	0.033486	
1.27	0.018703	
1.28	0.005090	
1.29		0.025424
1.30		0.009592

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REDUCED BARRIER INTEGRAL

Values of K

L*	0.050000	0.100000	0.150000	0.200000	0.250000
0.57	0.003374				
0.58	0.019403				
0.59	0.035673				
0.60	0.052194				
0.62	0.085917				
0.65	0.138248				
0.67	0.174278				
0.70	0.230009				
0.72	0.268262	0.008522			
0.73	0.287728	0.024762			
0.74	0.307411	0.041206			
0.75	0.327290	0.057848			
0.77	0.367729	0.091743			
0.80	0.429994	0.144106			
0.82	0.472369	0.180008	0.004530		
0.83	0.494052	0.198271	0.020897		
0.84	0.515943	0.216730	0.037453		
0.85	0.538046	0.235398	0.054200		
0.87	0.582831	0.273344	0.088277		
0.90	0.651649	0.331846	0.140865		
0.91	0.675022	0.351752	0.158792	0.019154	
0.92	0.698647	0.371891	0.176931	0.035893	
0.93	0.722517	0.392226	0.195262	0.052893	
0.94	0.746384	0.412840	0.213806	0.069949	
0.95	0.770838	0.433650	0.232565	0.087274	
0.97	0.820522	0.476002	0.270742	0.122536	0.005630
0.98	0.845766	0.497564	0.290180	0.140484	0.022446
0.99	0.871308	0.519297	0.309839	0.158640	0.039462
1.00	0.897211	0.541488	0.329748	0.177024	0.056685
1.01	0.923516	0.563906	0.349925	0.195638	0.074116
1.02	0.950280	0.586572	0.370379	0.214494	0.091760
1.03	0.977735	0.609786	0.391105	0.233592	0.109632
1.04	1.005980	0.633358	0.412163	0.252957	0.127734
1.05		0.657406	0.433580	0.272610	0.146081
1.06		0.682396	0.455398	0.292558	0.164686
1.07			0.477655	0.312825	0.183560
1.08			0.500674	0.333525	0.202732
1.09			0.524760	0.354657	0.222226
1.10				0.376352	0.242089
1.11				0.398895	0.262371
1.12					0.283181

REDUCED BARRIER INTEGRAL (Cont'd.)

Values of K

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L*	0.300000	0.350000	0.400000	0.450000	0.500000
1.03	0.006927				
1.04	0.024031				
1.05	0.041352				
1.06	0.058902				
1.07	0.076688				
1.08	0.094722	0.002398			
1.09	0.113026	0.019756			
1.10	0.131616	0.037358			
1.11	0.150518	0.055223			
1.12	0.169769	0.073365			
1.13	0.189428	0.091814	0.006727		
1.14	0.209567	0.110604	0.024524		
1.15	0.230344	0.129775	0.042618		
1.16	0.252098	0.149407	0.061042		
1.17		0.169624	0.079842		
1.18		0.190654	0.099083	0.018829	
1.19			0.118860	0.037331	
1.20			0.139393	0.056260	
1.21			0.161184	0.075710	
1.22				0.095839	0.019386
1.23				0.117029	0.038570
1.24					0.058395
1.25					0.079164

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REDUCED BARRIER INTEGRAL (Cont'd.)

Values of K

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L*	0.550000	0.600000
1.25	0.006318	
1.26	0.025909	
1.27	0.046365	
1.28	0.068392	
1.29		0.017766
1.30		0.039334

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