

# Efficient calculation of high-order semiclassical scattering phase shifts

Petri Pajunen

Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki 17, Finland

Robert J. Le Roy

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 14 June 1982; accepted 24 June 1982)

A quadrature procedure for the efficient computation of high-order semiclassical (or JWKB) scattering phase shifts for any smooth spherical potential is described and tested. In most situations this method yields phase shifts of "quantum mechanical accuracy" for almost the same computational effort associated with calculation of the familiar first-order JWKB phase shifts.

## I. INTRODUCTION

The efficient calculation of scattering phase shifts for spherical potentials is a ubiquitous problem associated with predictions of atomic and molecular collision processes. In principle, exact (numerical) quantum mechanical methods may always be used,<sup>1-3</sup> but they are computationally relatively time consuming and in some contexts become prohibitively expensive. The computationally inexpensive first-order phase integral or JWKB approximation is therefore a widely used alternative approach to this problem. However, while it can readily yield phase shifts of virtually any desired precision,<sup>4-6</sup> its lack of accuracy can be a source of significant error.

An obvious way of improving the accuracy of semiclassical phase shifts would be to use the higher-order phase integral approximations in place of the simple first-order method. Expressions for higher-order phase shifts have been known for some time,<sup>7-9</sup> but their use has been hindered by the lack of an efficient and generally applicable method for evaluating the requisite high-order phase integrals. This problem has now been solved by the development of simple and reliable procedures for evaluating high-order one-turning-point phase integrals of the type appearing in the phase shift expressions.<sup>10,11</sup> As is shown below, use of these techniques reduces the errors in semiclassical phase shifts by as much as several orders of magnitude, with little increase in computational effort.

It is commonly believed<sup>6</sup> that a significant improvement over the simple JWKB phase shifts is attained by incorporating a Langer-type correction<sup>12</sup> into the phase integral expressions. This question is also examined here, within both the first- and higher-order approximations.

## II. PHASE SHIFT EXPRESSIONS

In general, the semiclassical phase shift at energy  $E$  for orbital angular momentum quantum number  $l$  is given by

$$\eta_l(E) = \frac{1}{2} \int_{\Gamma} [q(r) - \kappa] dr + \kappa r_0 + (l + \frac{1}{2})\pi/2, \quad (1)$$

where  $\kappa^2 = 2\mu E/\hbar^2$ ,  $\mu$  is the reduced mass,  $q(r)$  is a function of  $\kappa^2$  and the effective central potential  $U(r)$  (see below),<sup>13-15</sup> and  $r_0$  is the classical turning point defined as the largest real zero of  $[E - U(r)]$ . As is illustrated schematically in Fig. 1,  $\Gamma$  is a nonclosed clockwise contour in the complex- $r$  plane which begins at  $r = +\infty$  on the lower lip of the branch cut emerging from  $r_0$ , encircles  $r_0$  and ends on the upper lip of this branch cut at  $r = +\infty$ .<sup>10</sup>

In the usual first-order phase integral or JWKB approximation,<sup>7,14</sup>  $q(r)$  is defined as

$$q^{(1)}(r) = \beta [E - U_l(r)]^{1/2}, \quad (2)$$

where  $\beta^2 = 2\mu/\hbar^2$ , and the effective central potential is

$$U_l(r) = V(r) + l(l+1)/\beta^2 r^2, \quad (3)$$

where  $V(r)$  is the rotationless potential and  $l(l+1)/\beta^2 r^2$  the centrifugal term. Since  $q^{(1)}(r)$  has no singularities on the real line, in this case  $\Gamma$  may be deformed onto

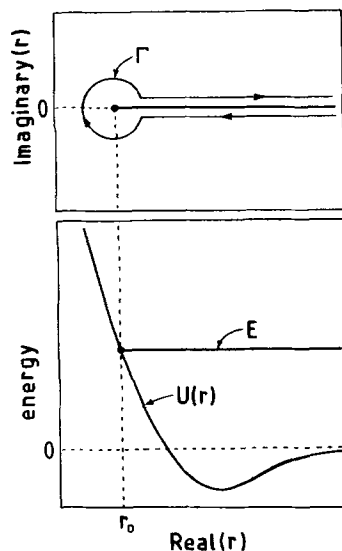


FIG. 1. Schematic representation of the potential energy curve (lower half) and integration contour  $\Gamma$  (upper half) associated with Eq. (1).

the real axis yielding the usual first-order phase shift expression<sup>4-7</sup>:

$$\eta_l^{(1)}(E) = \int_{r_0}^{\infty} [q^{(1)}(r) - \kappa] dr - \kappa r_0 + (l + \frac{1}{2})\pi/2. \quad (4)$$

In the higher-order semiclassical approximations,  $q(r)$  is a sum of terms associated with the various orders<sup>13</sup>

$$q(r) = q^{(1)}(r) + q^{(3)}(r) + q^{(5)}(r) + q^{(7)}(r) + \dots, \quad (5)$$

where, with primes denoting differentiation with respect to  $r$ , the third- and fifth-order terms are

$$q^{(3)}(r) = (1/48\beta) U_l'(r) / [E - U_l(r)]^{3/2}, \quad (6)$$

$$q^{(5)}(r) = (1/1536\beta^3) \{ 5 U_l'(r) U_l''(r) - 7 [U_l'(r)]^2 \} / [E - U_l(r)]^{5/2}, \quad (7)$$

and analogous expressions for higher-order terms may readily be generated in the manner described in Refs. 13 and 16. Since all of these higher-order  $q(r)$  functions have nonintegrable singularities at the turning point  $r_0$ , the contour  $\Gamma$  must avoid this point and hence cannot be collapsed onto the real line.

The Langer modification<sup>12</sup> of the ordinary phase integral approximation is based on a transformation introduced in order to allow the semiclassical wave functions to have the correct behavior at the origin for the Coulomb ( $r^{-1}$ ) and  $r^{-2}$  potentials. In first order, its effect is simply to replace  $l(l+1)$  by  $(l + \frac{1}{2})^2$  so that the phase integrand is

$$q_L^{(1)}(r) = \beta [E - U_L(r)]^{1/2}, \quad (8)$$

where the effective central potential is now

$$U_L(r) = V(r) + (l + \frac{1}{2})^2 / \beta^2 r^2, \quad (9)$$

and  $r_0$  is now defined as the zero of  $[E - U_L(r)]$ . When a Langer transformation is introduced consistently in higher order,<sup>8,14</sup> the resulting third- and fifth-order integrands become

$$q_L^{(3)}(r) = (1/48\beta) \{ U_L'(r) / [E - U_L(r)]^{3/2} + 6/r^2 [E - U_L(r)]^{1/2} \} \quad (10)$$

and

$$q_L^{(5)} = (1/1536\beta^3) \{ 5 U_L'(r) U_L''(r) - 7 [U_L'(r)]^2 \} / [E - U_L(r)]^{5/2} - 12/r^4 [E - U_L(r)]^{3/2} + 30 [U_L'(r)]^2 / r^2 [E - U_L(r)]^{3/2} - 24 U_L'(r) / r^2 [E - U_L(r)]^{5/2}. \quad (11)$$

Note, that in higher order, this transformation involves much more than the simple replacement of  $l(l+1)$  by  $(l + \frac{1}{2})^2$  in the expression for the centrifugal potential.

### III. EVALUATION OF THE PHASE INTEGRALS

All of the phase integrals appearing in the semiclassical phase shift expressions have the form

$$I_k(E) = \int_{\Gamma} dr f(r) / [E - U(r)]^{k+1/2}, \quad (12)$$

where  $k$  is an integer and  $f(r)$  some linear combination

of powers of  $[E - U(r)]$  and its derivatives. In first order,  $k = -1$  and  $f(r) = 1$ , and the integral is most efficiently evaluated<sup>6</sup> by collapsing the contour  $\Gamma$  onto the real line and using standard Gauss-Mehler quadrature formulas.<sup>17,18</sup> However, in the higher-order approximations  $k > 1$ , so that contour cannot be explicitly collapsed onto the real line since the integrand has a non-integrable singularity at  $r_0$ . The methods of Refs. 10 and 11 solve this problem by performing the integration in the complex plane implicitly, and yield simple quadrature formulas for  $I_k(E)$ ,

$$I_k = \sum_{m=1}^N w_m H(x_m) f(r_m) \{ (1 - x_m) / [E - U(r_m)] \}^{k+1/2}, \quad (13)$$

which only require knowledge of the functions  $f(r)$  and  $U(r)$  on the real line, while the weights  $w_m = w_m(k, N)$  and points  $x_m \in [0, 1]$  are known and may be taken from a published table<sup>10</sup> or generated implicitly by the integration routine.<sup>11</sup> The Jacobian factor  $H(x)$  is determined by the definition of the relationship between  $r$  and  $x$ ; the form of  $H(x)$  implied by three different definitions of  $r = r(x)$  is shown in Table I.

The simplest form of this method utilizes the change of variables  $x = r_0/r$  which transforms the interval  $r \in [r_0, \infty)$  onto  $x \in [0, 1]$ ; this is the first case considered in Table I. However, since most of the "interesting" behavior of the integrand is usually associated with small distances, say  $r \lesssim 2r_0$ , the number of function evaluations required to achieve a given level of accuracy will usually be minimized by subdividing the whole interval  $[r_0, \infty)$  into a segment  $[r_0, b]$  which contains the singularity, plus an interval  $[b, \infty)$  on which the whole of the integrand in Eq. (12) is smooth and well behaved. In this case, the portion of the contour associated with  $[b, \infty)$  may be collapsed onto the real line and (subject to the change of variable  $x = 2b/r - 1$ ) the corresponding contribution to the phase integral efficiently calculated using the normal Gauss-Legendre quadrature formula.<sup>18,19</sup> At the same time, subject to a change of variables of the type shown in the second and third entries in Table I, the portion of the integral associated with the interval  $[r_0, b]$  may be evaluated using Eq. (13). Note that in the limit  $b \rightarrow \infty$ , the second case considered in Table I becomes identical to the first one.

Another consideration which affects the number of required function evaluations is whether the contributions to the semiclassical phase shift in various orders are evaluated together or separately. The fact that the various contributions  $q^{(j)}(r)$  to the phase integral integrand are associated with different values of  $k$  ( $k = j + 2$ )

TABLE I. Jacobian functions  $H(x)$  associated with various definitions of the reduced integration variable  $x \in [0, 1]$ .

$r$ interval	$r = r(x)$	$H(x)$
$[r_0, \infty)$	$r_0/x$	$r_0/x^2$
$[r_0, b]$	$r_0 b / [(b - r_0)x + r_0]$	$r_0 b (b - r_0) / [(b - r_0)x + r_0]^2$
$[r_0, b]$	$b - (b - r_0)x$	$b - r_0$

TABLE II. At reduced energy  $\bar{E}=0.8$ , for  $LJ(12,6)$  potential with well-capacity parameter  $B_\sigma=125$ , quantal phase shifts  $\eta_l^{QM}$  and errors in semiclassical phase shifts  $\eta_l^{(j)}$  of order  $j$  calculated with ( $L$ ) and without inclusion of the Langer corrections.

$l$	$\eta_l^{QM}$	$[\eta_l^{(j)} - \eta_l^{QM}]$					
		$j=1$	$1L$	3	$3L$	5	$5L$
0	-6.714 1896	0.042 6282	0.030 8050	0.000 0288	0.000 0134	-0.000 0036	-0.000 0036
5	-0.298 3421	0.044 7743	0.032 6561	0.000 0276	0.000 0095	-0.000 0057	-0.000 0057
10	3.519 4928	0.052 9134	0.039 7892	0.000 0538	0.000 0223	0.000 0278	0.000 0279
15	3.804 5944	0.074 9558	0.058 3668	-0.018 5914	-0.018 7822	-0.017 8876	-0.017 8788
20	0.465 9448	0.002 3206	-0.008 0554	-0.000 1438	-0.000 1666	0.000 0202	0.000 0191
25	0.141 7075	0.006 6581	-0.001 1825	-0.000 0084	-0.000 0093	0.000 0000	-0.000 0001
30	0.056 6391	0.006 1639	-0.000 3126	-0.000 0017	-0.000 0015	0.000 0000	0.000 0000
35	0.026 3232	0.005 4388	-0.000 1055	-0.000 0006	-0.000 0004	0.000 0000	0.000 0000
40	0.013 5798	0.004 8119	-0.000 0416	-0.000 0003	-0.000 0001	0.000 0000	0.000 0000
45	0.007 5763	0.004 2995	-0.000 0183	-0.000 0002	0.000 0000	0.000 0000	0.000 0000
50	0.004 4945	0.003 8805	-0.000 0088	-0.000 0001	0.000 0000	0.000 0000	0.000 0000

would appear to suggest that the integral for each order  $j$  should be evaluated separately. However, only a fraction as many function evaluations are required if the whole function  $q(z)$  is expressed with a common denominator  $[E - U(r)]^{k+1/2}$  corresponding to the highest-order term included in the integrand, and the integral evaluated using the appropriate version of Eq. (13). This procedure causes no significant loss of accuracy, since its only effect is to introduce integer powers of the well-behaved function  $[E - U(r)]$  into the integrand numerator  $f(r)$ . For example, in fifth order this would cause the phase shift to be evaluated as a  $k=3$  integral with

$$f(r) = \beta [E - U(r)]^4 + (1/48\beta) U''(r) [E - U(r)]^2 + (1/1536\beta^3) \{5U'(r)U''(r) - 7[U''(r)]^2\}. \quad (14)$$

#### IV. TEST OF HIGH-ORDER SEMICLASSICAL PHASE SHIFTS

The present procedure for evaluating high-order phase shifts was tested using an  $LJ(12,6)$  potential

$$V(r) = D_e [(\sigma/r)^{12} - (\sigma/r)^6], \quad (15)$$

whose well-capacity parameter  $B_\sigma = 2\mu D_e \sigma^2 / \hbar^2 = 125$

corresponds roughly to that for  $\text{Ne}_2$  or for the spherical part of the  $\text{D}_2\text{-Ar}$  interaction potential. "Exact" quantal phase shifts for this model system were computed using the method of Ref. 3. While quite straightforward to perform, calculations which yield quantal phase shifts of very high accuracy can be quite time consuming. In the present work, 20 000–30 000 integration mesh points were required to ensure that the resulting phase shifts were converged to seven decimal places. In contrast, equivalent high-order semiclassical phase shifts converged to seven decimal places required only 20–30 quadrature mesh points (!), while results of lower precision require even fewer points. For example, four decimal place convergence for the cases considered below was typically achieved using only 10–15 points.

For the four reduced energies  $\bar{E} = E/D_e = 0.8, 1.8, 3.2,$  and  $7.2$ , and a wide range of values of the partial wave index  $l$ , Tables II–V list the (exact) quantal phase shifts  $\eta_l^{QM}(E)$  and the errors in the corresponding semiclassical phase shifts  $\eta_l^{(j)}(E)$  of order  $j=1, 3,$  and  $5$  evaluated both with ( $L$ ) and without inclusion of the Langer corrections. It is immediately apparent that the errors in the first-order (1) and first-order-Langer (1L) results are sufficiently large that cross sections

TABLE III. At reduced energy  $\bar{E}=1.8$ , as in Table II.

$l$	$\eta_l^{QM}$	$[\eta_l^{(j)} - \eta_l^{QM}]$					
		$j=1$	$1L$	3	$3L$	5	$5L$
0	-12.048 8682	0.033 8833	0.025 2903	0.000 0499	0.000 0419	-0.000 0006	-0.000 0007
5	-5.233 8895	0.034 9626	0.026 2547	0.000 0565	0.000 0476	-0.000 0008	-0.000 0009
10	-0.223 5468	0.038 4951	0.029 4404	0.000 0836	0.000 0714	-0.000 0019	-0.000 0020
15	2.730 6070	0.047 9084	0.038 1038	0.000 2064	0.000 1821	-0.000 0197	-0.000 0202
20	2.878 5538	0.101 9973	0.090 2789	0.009 2090	0.009 0586	0.003 6205	0.003 5798
25	0.807 4122	0.001 5728	-0.007 0591	0.000 4222	0.000 4123	0.000 0768	0.000 0793
30	0.297 0522	0.004 9187	-0.001 7291	-0.000 0033	-0.000 0045	0.000 0004	0.000 0004
35	0.135 0941	0.005 0458	-0.000 5536	-0.000 0016	-0.000 0017	0.000 0000	0.000 0000
40	0.069 1684	0.004 6609	-0.000 2139	-0.000 0006	-0.000 0005	0.000 0000	0.000 0000
45	0.038 4708	0.004 2336	-0.000 0936	-0.000 0003	-0.000 0002	0.000 0000	0.000 0000
50	0.022 7902	0.003 8489	-0.000 0449	-0.000 0002	-0.000 0001	0.000 0000	0.000 0000

TABLE IV. At reduced energy  $\bar{E}=3.2$ , as in Table II.

$l$	$\eta_l^{QM}$	$[\eta_l^{(j)} - \eta_l^{QM}]$					
		$j=1$	$1L$	$3$	$3L$	$5$	$5L$
0	-16.931 6885	0.028 0721	0.021 2618	0.000 0430	0.000 0384	0.000 0003	0.000 0002
5	-9.898 9013	0.028 6762	0.021 8091	0.000 0474	0.000 0425	0.000 0003	0.000 0003
10	-4.269 7969	0.030 5131	0.023 4827	0.000 0632	0.000 0572	0.000 0006	0.000 0005
15	-0.153 3269	0.034 4831	0.027 1427	0.000 1129	0.000 1042	0.000 0020	0.000 0018
20	2.216 0456	0.043 8760	0.035 9762	0.000 3666	0.000 3494	0.000 0254	0.000 0248
25	2.347 0796	0.066 9430	0.058 1054	-0.000 3760	-0.000 3888	-0.000 9599	-0.000 9492
30	1.004 8161	0.005 4855	-0.001 7199	0.000 4871	0.000 4942	-0.000 0233	-0.000 0216
35	0.439 2100	0.004 0980	-0.001 6626	0.000 0107	0.000 0100	0.000 0008	0.000 0009
40	0.221 3946	0.004 2626	-0.000 6720	-0.000 0004	-0.000 0005	0.000 0000	0.000 0000
45	0.122 3503	0.004 0572	-0.000 2956	-0.000 0005	-0.000 0004	0.000 0000	0.000 0000
50	0.072 2692	0.003 7642	-0.000 1418	-0.000 0003	-0.000 0002	0.000 0000	0.000 0000

calculated from those phase shifts would be of dubious accuracy. However, the analogous errors in the higher-order phase shifts are typically several orders of magnitude smaller, so that there can be little doubt about the accuracy of the cross sections they yield.

In each of Tables II–V there is a range of  $l$  values for which the errors in the semiclassical phase shifts go through a local maximum. These are the  $l$  values for which the orbiting resonances associated with the  $\nu=0$  vibrational level of this potential lie closest to the chosen fixed  $\bar{E}$  values. To verify this statement, the energies and widths of these orbiting resonances for  $11 \leq l \leq 45$  (for  $l < 11$  this resonance becomes a truly bound level) were determined by calculating the position and height of the maximum in the collisional time delay function.<sup>20</sup> The resulting reduced energies  $\bar{E}_r$  and widths  $\bar{\Gamma}$  of the resonances lying closest to the four chosen energies ( $\bar{E}=0.8, 1.8, 3.2$ , and  $7.2$ ) are listed in Table VI, while some of the corresponding effective potentials  $\bar{U}_l(r) = U_l(r)/D_e$  and their associated resonance energies  $\bar{E}_r(l)$  are plotted in Fig. 2. It is interesting to see that this resonance is still a discernable phenomenon at very high  $l$  values where the effective centrifugally distorted potential shows little apparent memory of

the existence of a well in the supporting potential energy curve.

It is of course no surprise that simple one-turning-point semiclassical phase shift calculations such as those reported here encounter difficulties in the neighborhood of a resonance. However, it is gratifying to see that, at least at energies above an identifiable centrifugal barrier maximum (here, for  $\bar{E} > 0.8$ ) the substantial improvement in accuracy of the higher-order phase shifts is maintained even at a resonance where this error term has a local maximum. The only situations in which the higher-order predictions are no better (and perhaps much worse) than the first-order values is for energies either close to a barrier maximum, or near a resonance which lies at or below a barrier maximum. The problem there is simply that the simple one-turning-point phase shift formula of Eq. (1) is no longer valid in any order. A generalization of Eq. (1) appropriate to this three-turning-point case is well known in first order<sup>21,22</sup> and has been consistently derived for arbitrary order.<sup>15</sup> However, in practice it is often as convenient to perform exact quantal calculations at these low energies where a relatively large numerical integration mesh can be used, so the semiclassical

TABLE V. At reduced energy  $E=7.2$ , as in Table II.

$l$	$\eta_l^{QM}$	$[\eta_l^{(j)} - \eta_l^{QM}]$					
		$j=1$	$1L$	$3$	$3L$	$5$	$5L$
0	-25.935 8950	0.020 8492	0.015 9699	0.000 0228	0.000 0209	0.000 0002	0.000 0002
5	-18.668 8731	0.021 0861	0.016 1864	0.000 0240	0.000 0221	0.000 0002	0.000 0002
10	-12.392 3771	0.021 7593	0.016 8033	0.000 0278	0.000 0256	0.000 0003	0.000 0003
15	-7.141 8359	0.023 0019	0.017 9479	0.000 0359	0.000 0334	0.000 0005	0.000 0004
20	-2.981 7353	0.025 1062	0.019 9020	0.000 0536	0.000 0504	0.000 0010	0.000 0009
25	-0.017 5203	0.028 6740	0.023 2505	0.000 0946	0.000 0902	0.000 0026	0.000 0025
30	1.591 5407	0.034 3082	0.028 5887	0.000 1319	0.000 1271	-0.000 0024	-0.000 0024
35	1.738 1670	0.031 0721	0.025 1942	-0.000 6034	-0.000 5891	0.000 0212	0.000 0216
40	1.093 6533	0.008 4147	0.003 1775	0.000 1242	0.000 1312	-0.000 0107	-0.000 0107
45	0.620 5350	0.003 8716	-0.000 6319	0.000 0249	0.000 0253	0.000 0003	0.000 0004
50	0.367 1304	0.003 4223	-0.000 5565	0.000 0030	0.000 0030	0.000 0001	0.000 0001

TABLE VI. Reduced energies  $\bar{E}_r = E_r/D_e$  and widths  $\bar{\Gamma} = \Gamma/D_e$  for  $v=0$  resonances of the  $B_0=125$  LJ(12, 6) potential which lie closest to the energies of Tables II–V.

$\bar{E}$	$l$	$\bar{E}_r(v=0, l)$	$\bar{\Gamma}(v=0, l)$
0.8	16	0.712	0.160
	17	0.859	0.238
1.8	22	1.731	0.866
	23	1.933	1.045
3.2	28	3.071	2.245
	29	3.324	2.255
7.2	41	7.016	8.351
	42	7.378	9.035

three-turning-point problem is not considered here.

The results in Tables II–V indicate that use of the Langer transformation usually leads to some improvement in the first-order phase shifts, particularly at high  $l$ , where the centrifugal term dominates the potential. However, except when the phase shift is approaching zero at large  $l$ , this improvement is insignificant relative to that attained on including the higher-order terms in the phase integral, while in higher order the use of the Langer correction involves more computation but yields no real improvement in accuracy.

## V. DISCUSSION AND CONCLUSIONS

The results presented above show that the inaccuracy of ordinary first-order or first-order-Langer semiclassical phase shifts can be a serious source of error. However, they also show that much of this error can be removed at very little additional computational cost by including the higher-order terms in the semiclassical phase integrals. Moreover, even for the rather extreme (i.e., small  $B_0$ ) model problem considered here, it seems clear that except at a barrier maximum or near a sharp resonance, the improvement in accuracy achieved using the third- or fifth-order version of the simple one-turning-point formula of Eq. (1) is sufficient to make quantal phase shift calculations redundant.

In general, the errors in the first-order results are expected to be relatively smaller for systems corresponding to larger values of the well-capacity parameter  $B_0$ . In particular, if the dominant source of error in phase shifts of order  $j$  is attributed to the first neglected higher-order term, Eqs. (1)–(7) show that the error in the first-order phase shifts will be proportional to  $(B_0)^{-1}$ . By the same argument, the errors in the third- and fifth-order phase shifts scale as  $(B_0)^{-2}$  and  $(B_0)^{-3}$ , respectively. Thus, while the magnitude of errors in first-order phase shifts should decrease with increasing well-capacity parameter, the improvement in accuracy attained on including higher-order terms increases even more. Since the higher-order calculations require very little additional computational effort, there would now appear to be little point in *ever* calculating ordinary first-order phase shifts.<sup>23</sup>

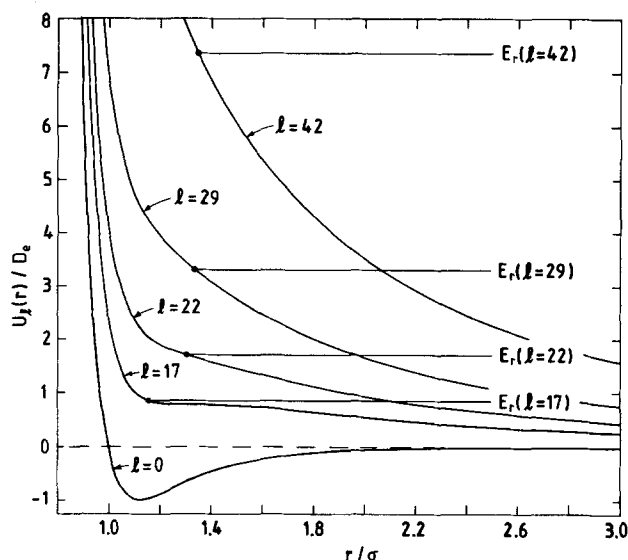


FIG. 2. Reduced effective potentials  $\bar{U}_l(r)$  and energies  $\bar{E}_r(l)$  of the  $v=0$  orbiting resonance associated with the  $l=17, 22, 29$ , and 42 partial waves for the given model potential.

## ACKNOWLEDGMENTS

One of us (R.J.L.) is grateful to Dr. M. S. Child and to the Theoretical Chemistry Department of the University of Oxford for their hospitality and the provision of computational facilities which facilitated the early part of this work. P. P. is also grateful to the Natural Sciences and Engineering Research Council of Canada for the award of an International Scientific Exchange Award in 1981.

- <sup>1</sup>R. B. Bernstein, *J. Chem. Phys.* **33**, 795 (1960).
- <sup>2</sup>R. J. Munn, E. A. Mason, and F. J. Smith, *J. Chem. Phys.* **41**, 3978 (1964).
- <sup>3</sup>J. W. Hepburn and R. J. Le Roy, *Chem. Phys. Lett.* **57**, 304 (1978).
- <sup>4</sup>M. Kennedy and F. J. Smith, *Mol. Phys.* **13**, 443 (1967).
- <sup>5</sup>R. T. Pack, *J. Chem. Phys.* **60**, 633 (1974).
- <sup>6</sup>J. S. Cohen, *J. Chem. Phys.* **68**, 1841 (1978).
- <sup>7</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), Sec. 10.3.
- <sup>8</sup>(a) C. F. Curtiss and R. E. Powers Jr., *J. Chem. Phys.* **40**, 2145 (1964); (b) S.-I. Choi and J. Ross, *ibid.* **40**, 2151 (1964); (c) H. T. Wood and C. F. Curtiss, *ibid.* **41**, 1167 (1964).
- <sup>9</sup>S. S. Wald and P. Lu, *J. Chem. Phys.* **61**, 4680 (1974).
- <sup>10</sup>P. Pajunen, *J. Chem. Phys.* **73**, 6232 (1980).
- <sup>11</sup>J. Luppi and P. Pajunen, *J. Chem. Phys.* **77**, 1505 (1982).
- <sup>12</sup>R. E. Langer, *Phys. Rev.* **57**, 669 (1937).
- <sup>13</sup>N. Fröman, *Ark. Fys.* **32**, 541 (1966).
- <sup>14</sup>N. Fröman and P.-O. Fröman, *Nuovo Cimento B* **20**, 121 (1974).
- <sup>15</sup>N. Fröman, in *Semiclassical Methods in Scattering and Spectroscopy*, edited by M. S. Child (Reidel, Dordrecht, 1980), Chap. I, p. 1.
- <sup>16</sup>(a) N. Fröman and P. O. Fröman, *Nucl. Phys. A* **147**, 606 (1970); (b) J. A. Campbell, *J. Comput. Phys.* **10**, 308 (1972);

(c) J. A. Campbell, *J. Phys. A* **12**, 1149 (1979).

<sup>17</sup>Subject to the change of variables  $x=r_0/r$ , Eqs. (25.4.34) or (25.4.36) of Ref. 18.

<sup>18</sup>M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1968).

<sup>19</sup>Equation (25.4.29) of Ref. 18.

<sup>20</sup>R. J. Le Roy and R. B. Bernstein, *J. Chem. Phys.* **54**, 5114 (1971); (b) R. J. Le Roy and W.-K. Liu, *ibid.* **69**, 3622 (1978).

(1978).

<sup>21</sup>K. W. Ford, D. L. Hill, M. Wakano, and J. A. Wheeler, *Ann. Phys.* **7**, 239 (1959).

<sup>22</sup>J. N. L. Connor, in *Semiclassical Methods in Scattering and Spectroscopy*, edited by M. S. Child (Reidel, Dordrecht, 1980), Chap. 2, p. 45.

<sup>23</sup>Listings of the programs used to generate the results in Tables II-V may be obtained from the authors on request.