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Error cancellation in the semiclassical calculation of the scattering length

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Abstract. We investigate the effects of two approximations concerning long range dispersion forces that are made in the derivation of the semiclassical formula for the scattering length of a pair of neutral atoms. We demonstrate numerically, using a published model interaction potential for a pair of Cs atoms in the $^3\Sigma_u^+$ molecular state, that the subsequent long range errors tend to cancel and we show, from an approximate analytical relationship, that the first order errors do indeed largely cancel. We suggest a hybrid method that combines quantum mechanical and semiclassical calculations. We explore its use in finding the scattering lengths of ^{7}Li atoms and ^{133}Cs atoms interacting via the $X^1\Sigma^+$ and $a^3\Sigma^+$ molecular potentials and we use it to demonstrate that the semiclassical formula fails for cold collisions of H atoms in the $X^1\Sigma_g^+$ molecular state because of the long range errors rather than because of inadequacies in describing the motion over the potential well semiclassically.

1 Introduction

The scattering length, a, determines the low energy limit of the cross section for elastic collisions [1]. The semiclassical expression for it that was given by Gribakin and Flambaum [2] has proved to be remarkably successful in predictions for various neutral atom pairs. Apart from its ability to provide accurate scattering data for cold collisions its analytic nature makes it very valuable in predicting changes in scattering length in response to changes in the masses of the colliding atoms, such as occur when different isotopes are considered, and in response to changes in their mutual interaction. The interaction potential $V(R)$ of such a pair typically consists of a well, which supports many bound states on account of the reduced mass being large, and a long range tail

$$V_{\mathrm{L}}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots \qquad (1)$$

where R is the atomic separation and $C_6, \dots$ are the van der Waals dispersion coefficients. In this discussion we retain only the first three dispersion terms because their coefficients are the most widely available; the conclusion is not altered by this restriction. In a quantum mechanical calculation a wave function is propagated across the well into the tail; the wave function oscillates rapidly in recognition of the bound states and the numerical propagation is tedious. The semiclassical formula has the advantage that no such rapidly oscillating function is required in its evaluation. However, in their derivation of the semiclassical formula, Gribakin and Flambaum [2] made two approximations in each of which they assumed that, for some atomic separations R, the contribution $-C_8/R^8 - C_{10}/R^{10}$ to $V_{\mathrm{L}}(R)$ could be ignored as being less influential than the leading van der Waals term $-C_6/R^6$.

In this paper we demonstrate numerically for the model potential used by Gribakin and Flambaum [2] (for the zero energy scattering of ^{133}Cs atoms by ^{133}Cs atoms interacting via the $^3\Sigma_u^+$ molecular potential) that the errors introduced by their approximations are not trivial but that they tend to cancel.

We establish, with numerical evidence, some approximations for certain integrals involving Bessel functions of order $\pm\frac{1}{4}$ and show that the first order errors cancel within these approximations.

We explore a hybrid scheme that combines a semiclassical formula with a quantum mechanical calculation as a method that avoids the errors and removes the need to propagate a rapidly oscillating numerical wave function across the deepest part of the potential well. We illustrate the hybrid method with a calculation of scattering lengths for collisions of ^{7}Li atoms with ^{133}Cs interacting via the $X^1\Sigma^+$ potential of the LiCs dimer. We demonstrate that the agreement between semiclassical, hybrid and quantum mechanical calculations breaks down near the zero energy resonance that is present for collisions of ^{7}Li atoms with ^{133}Cs interacting via the $a^3\Sigma^+$ potential. We argue that the failure of the semiclassical formula to

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predict the scattering length for pairs of H atoms interacting via the $X^1\Sigma_g^+$ potential is mainly attributable to the errors in accounting for the long range dispersion forces and not to errors induced by use of semiclassical theory to describe the motion over the potential well.

2 Errors

The semiclassical formula appropriate to a pair of atoms with reduced mass μ interacting via a long range potential with leading term proportional to $-C_6/R^6$ is [2]

$$a_{\rm SC} = \overline{a}\left\{1 - \tan\left[\int_{R_0}^{R}\frac{\sqrt{-2\mu V(R)}}{\hbar}dR - \frac{\pi}{8}\right]\right\} \qquad (2)$$

where $\overline{a}$ is the mean scattering length, $2\pi\hbar$ is Planck's constant and R_0 is the classical turning point of the zero energy wave function. The mean scattering length is

$$\overline{a} = \frac{2\pi\gamma_6}{[\Gamma(1/4)]^2} \qquad (3)$$

where Γ denotes the gamma function and

$$\gamma_n = \sqrt[n-2]{\frac{2\mu C_n}{\hbar^2}}. \qquad (4)$$

In a full quantum mechanical treatment the radial part $\phi(R)$ of the zero energy wave function, normalised so that

$$\phi(R) \to (R-a)/R \quad \text{as } R \to \infty, \qquad (5)$$

is given at large R by

$$\phi(R) = \sqrt{\frac{\pi\overline{a}}{2R}}\left[J_{-\frac{1}{4}}(x) - \frac{a}{\sqrt{2\overline{a}}}J_{\frac{1}{4}}(x)\right] \qquad (6)$$

where $J_{\pm\frac{1}{4}}(x)$ denote Bessel functions of the first kind [3] and $x = \gamma_6^2/2R^2$; in Table 1 we show values of x for various values of R for the three numerical examples that we consider.

Gribakin and Flambaum [2] derived formula (2) by matching a semiclassical wave function that accounts adequately for the motion within the potential well to function (6) which is exact asymptotically. In obtaining a formula that is independent of the interatomic distance at which the matching is made they made two approximations involving the higher order dispersion terms $-C_8/R^8 + \ldots$; the errors thus induced and their approximate cancellation are the objects of this discussion.

We summarise the derivation of formula (2) as follows; the reader is directed to the original paper of Gribakin and Flambaum [2] for the details. First the semiclassical representation of the wave function is used for small to intermediate values of R. Then it is matched to expression (6) for large R. The separation R^* for matching is chosen to ensure that the semiclassical form is indeed accurate for separations smaller than R^* (typically over the well), which requires that the de Broglie wavelength

Table 1. Miscellaneous data.

^{133}Cs-^{133}Cs		^{7}Li-^{133}Cs		H-H	
R (bohr)	$x^{\rm a}$	R (bohr)	$x^{\rm a}$	R (bohr)	$x^{\rm a}$
40	13	20	11	2.0	14
50	8.3	25	6.9	2.5	8.9
55	6.8	27	5.9	3.0	6.2
60	5.7	30	4.8	3.5	4.5
70	4.2	35	3.5	4.0	3.5
80	3.2	40	2.7	4.5	2.7
90	2.6	45	2.1	5.0	2.2
100	2.1	50	1.7	5.5	1.8
$R^{\rm b}_{\rm min}$	$R^{\rm c}_{\rm max}$	$R^{\rm b}_{\rm min}$	$R^{\rm c}_{\rm max}$	$R^{\rm b}_{\rm min}$	$R^{\rm c}_{\rm max}$
(bohr)					
12.5	117	10.2	53.6	4.38	6.03
$x^{\rm d}_{\rm min}$	$x^{\rm e}_{\rm max}$	$x^{\rm d}_{\rm min}$	$x^{\rm e}_{\rm max}$	$x^{\rm d}_{\rm min}$	$x^{\rm e}_{\rm max}$
1.5	3.2	1.5	2.2	1.5	2.9

[a] $x = \frac{\gamma_6^2}{2R^2}$. [b] Equation (12). [c] Equation (7). [d] Equation (8). [e] Equation (13).

changes very slowly with R [2], and to ensure that the Bessel functions are represented to sufficient accuracy by their trigonometric asymptotic expressions for large argument [3]. Provided that R^* is in the dispersion region of the potential these conditions are met simultaneously when R^* is small enough that

$$R^* \ll R_{\rm max} = \frac{\gamma_6}{\sqrt{3}}. \qquad (7)$$

In terms of x condition (7) is

$$x^* \gg x_{\rm min} = \frac{3}{2}. \qquad (8)$$

The semiclassical function used by Gribakin and Flambaum [2] is

$$\chi(R) = \frac{C}{R\sqrt{p(R)}}\cos\left[\int_{R_0}^{R}\frac{p(R')}{\hbar}dR' - \frac{\pi}{4}\right] \text{ for } R > R_0 \qquad (9)$$

where C is a constant, $p(R) = \sqrt{-2\mu V(R)}$ is the local momentum and R_0 is the classical turning point. The radial Schrödinger wave equation is all but satisfied by the function $\chi(R)$ except for a term which adds an amount in error to the potential; this error is

$$\delta V(R) = \frac{\hbar^2}{2\mu}\left\{3\left[\frac{1}{2p(R)}\frac{dp(R)}{dR}\right]^2 - \frac{1}{2p(R)}\frac{d^2p(R)}{dR^2}\right\}. \qquad (10)$$

At separations where the potential is dominated by the leading dispersion term expression (10) can be simplified and we find that the potential is changed by a *relative* amount $3R^4/4\gamma_6^4$ which is much smaller than 1/12 when condition (7) is replaced by equality.

There are errors in amplitude and phase when the Bessel functions are represented by the simple trigonometric asymptotic functions as [3]

$$J_{\pm\frac{1}{4}}(x) \approx \sqrt{\frac{2}{\pi x}} \cos\left(x \mp \frac{\pi}{8} - \frac{\pi}{4}\right). \tag{11}$$

We need to represent the function $\phi(R)$ of equation (6) and its derivative. From the asymptotic forms of the Bessel functions [3] we see that the biggest magnitudes of the leading relative amplitude and phase errors are $13R^4/16\gamma_6^4$ and $13R^4/8\gamma_6^4$ respectively. These are much smaller than $13/144 \approx 1/12$ and $13/72 \approx 1/6$ respectively when condition (7) is replaced by equality.

However in matching expression (9) to the long range form of the wave function (6) the implicit approximation of ignoring the remaining dispersion terms is made; to be able to ignore $-C_8/R^8 + \ldots$ we need R^* to be large enough to meet the condition

$$R^* \gg R_{\min} = \sqrt{\frac{C_8}{C_6}}. \tag{12}$$

In terms of x condition (12) is

$$x^* \ll x_{\max} = \frac{1}{2}\left(\frac{\gamma_6}{\gamma_8}\right)^2. \tag{13}$$

Often C_8 is considerably larger than C_6 so that conditions (7) and (12) conflict. If we stipulate that, in this context, '$\ll$' of condition (7) means 'less than one tenth of', the subsequent relative discrepancy in the potential is smaller than 0.00001 and the relative errors in the amplitudes and phases of the trigonometric representations of the Bessel functions are smaller than 0.00002; we note that some caution is needed in interpreting the relative phase errors since the trigonometric functions themselves are limited to ± 1. If we stipulate that '$\gg$' of condition (12) means 'greater than ten times', the relative error made by ignoring the higher order dispersion terms is much larger being limited by 0.01.

In Table 1 we show the values of $R_{\min}$ and $R_{\max}$ of equations (7) and (12), for the three numerical examples we discuss later. With the stipulation that '$\ll$' means 'less than one tenth of' and '$\gg$' means 'greater than ten times' in the conditions for R^*, we see that these conditions are in conflict for the first two examples; with no such stipulation they are clearly in conflict for H-H collisions where the semiclassical formula fails completely. We also show the values of $x_{\min}$ and $x_{\max}$ of equations (13) and (8); the range of x is much smaller.

It is clearly easier to ensure that the semiclassical representation and the Bessel functions are accurate in the dispersion region than it is to be able to neglect the higher order dispersion terms when matching the semiclassical function (9) to the asymptotic function (6). Henceforth we shall assume that, in a calculation, R^* is chosen to make the semiclassical and Bessel errors acceptably small, leaving the penalty of a possible larger error caused by neglect of the higher order dispersion terms. We focus on this 'dispersion' error. We show that it has two sources and we refer below to the subsequent errors as 'first' and 'second' errors.

2.1 First error

The source of the first error is the matching of the semiclassical wave function to function (6) which is exact only when the interaction is represented by the leading dispersion term $-C_6/R^6$. The error is

$$\delta_1(R^*) = a - \tilde{a}(R^*) \tag{14}$$

where a is the scattering length for the full potential $V(R)$ and $\tilde{a}(R^*)$ is the scattering length for the potential defined by

$$\tilde{V}(R^*;R) = \begin{array}{ll} V(R) & \text{if } R \le R^* \\ -C_6/R^6 & \text{if } R > R^* \end{array} \tag{15}$$

which depends on R^* as a parameter and is the potential $V(R)$ modified at long range to include only the leading dispersion term. This error is negligible only when condition (12) is met.

2.2 Second error

The source of the second error is the further approximation needed to enable a formula that is independent of the matching separation R^* to be found. The approximation is that of reinstating the original potential which, for matching the radial wave function to expression (6) had been replaced by the modified potential $\tilde{V}(R^*;R)$, in the quadrature on the right hand side of equation (2). The error is

$$\delta_2(R^*) = a_{\rm SC} - \tilde{a}_{\rm SC}(R^*) \tag{16}$$

where $a_{\rm SC}$ is the semiclassical scattering length for the original potential and $\tilde{a}_{\rm SC}(R^*)$ is the semiclassical scattering length for the modified potential $\tilde{V}(R^*;R)$; both are calculated from formula (2). This error also is negligible only when R^* is large enough that condition (12) is met.

From equations (2) and (16) we find

$$\delta_2(R^*) = -\overline{a}\left\{\tan\left[\int_{R^*}^{\infty} \frac{\sqrt{-2\mu V_{\rm L}(R)}}{\hbar} dR - \frac{\pi}{8}\right] - \tan\left(\int_{R^*}^{\infty} \frac{\sqrt{2\mu C_6 R^{-6}}}{\hbar} dR - \frac{\pi}{8}\right)\right\} \tag{17}$$

where $V_{\rm L}(R)$ is defined by equation (1).

Provided that R^* lies where the well-depth is sufficiently large that the motion can be described adequately by semiclassical theory

$$\tilde{a}(R^*) \approx \tilde{a}_{\rm SC}(R^*) \tag{18}$$

and then equations (14) and (16) imply that the scattering length a is

$$a = a_{\rm SC} + \delta_1(R^*) - \delta_2(R^*). \tag{19}$$

We demonstrate below, with a numerical example, that the error terms in equation (19) tend to cancel.

2.3 Accumulated scattering lengths

In the variable phase approach for calculating scattering lengths quantum mechanically [4,5] an *accumulated* scattering length $a(R)$ is calculated by solving the first order differential equation

$$\frac{da(R)}{dR} = \frac{2\mu}{\hbar^2} V(R)\,[R - a(R)]^2 \tag{20}$$

and the complete scattering length is $a = a(\infty)$.

The accumulated scattering length at R is equal to $R - 1/u(R)$ where $u(R)$ is the log-derivative of R times the radial wave function at R [6]. Following differentiation with respect to R of $R \times \chi(R)$, where $\chi(R)$ is given by equation (9), we find that the semiclassical accumulated scattering length is

$$a_{\rm SC}(R) = R + \left\{ \frac{\mathcal{V}(R)}{4} + \frac{\sqrt{-2\mu V(R)}}{\hbar} \times \tan\left[\int_{R_0}^{R} \frac{\sqrt{-2\mu V(R)}}{\hbar} dR - \frac{\pi}{4} \right] \right\}^{-1} \tag{21}$$

where $\mathcal{V}(R)$ is the log-derivative of $V(R)$. Equation (21) becomes

$$a_{\rm SC}(R) = R \left\{ \frac{1 - 4x \tan\left[\int_{R_0}^{R} \frac{\sqrt{-2\mu V(R)}}{\hbar} dR - \frac{\pi}{4} \right]}{3 - 4x \tan\left[\int_{R_0}^{R} \frac{\sqrt{-2\mu V(R)}}{\hbar} dR - \frac{\pi}{4} \right]} \right\} \tag{22}$$

when the interaction is dominated by the leading dispersion term. However we found this expression (22) is insufficiently precise to yield good agreement between calculated quantal and semiclassical accumulated scattering lengths but, nonetheless, it proved useful in providing a check on the numerical procedure that we used to calculate $\mathcal{V}(R)$.

When the potential is represented by the leading dispersion term $-C_6/R^6$ alone for $R > R^*$ the complete scattering length a can be fitted to the accumulated scattering length $a(R^*)$, $= a^*$ say, from the formula

$$a = \overline{a}\sqrt{2} \left[\frac{4x^*(R^* - a^*) J'_{-\frac{1}{4}}(x^*) + (R^* + a^*) J_{-\frac{1}{4}}(x^*)}{4x^*(R^* - a^*) J'_{\frac{1}{4}}(x^*) + (R^* + a^*) J_{\frac{1}{4}}(x^*)} \right] \tag{23}$$

where $J'_{\pm\frac{1}{4}}(x)$ denote the derivatives of the Bessel functions with respect to argument. This formula was given in a slightly different form by Smytkowski [6]. Substitution of $a_{\rm SC}(R^*)$ from equation (22) for a^* in equation (23) and representation of the Bessel functions by equation (11) leads to the semiclassical formula (2). We see that if the numerator of the right hand side of equation (23) is close to zero then the complete scattering length can be sensitive to changes in the accumulated scattering length. In particular at separations where equation (11) gives a good approximation to $J_{\frac{1}{4}}(x)$ the scattering length can be ill-conditioned when

$$\tan\left(x^* + \frac{\pi}{8}\right) = 4x^* \frac{R^* - a^*}{R^* + a^*}. \tag{24}$$

2.4 Numerical demonstration

We consider the scattering lengths for collisions of pairs of ground state ^{133}Cs atoms interacting via the $^3\Sigma_{\rm u}^+$ molecular potential. This is the model problem used by Gribakin and Flambaum [2] when they introduced the semiclassical formula (2). We use the analytic potential that was adopted by them which is

$$V(R) = \frac{1}{2} B R^{\alpha} \exp(-\beta R) - \left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} \right) f_{\rm c}(R) \tag{25}$$

where $f_{\rm c}(R)$ is unity if $R > R_{\rm c}$ and is

$$f_{\rm c}(R) = \exp\left[-\left(\frac{R_{\rm c}}{R} - 1 \right)^2 \right] \tag{26}$$

otherwise; in equations (25) and (26) B, α and β are exchange parameters, C_6, C_8 and C_{10} are dispersion coefficients and $R_{\rm c}$ is a cut-off radius, whose values in atomic units are 0.0016, 5.53, 1.072, 7020, 1.1×10^6, 1.7×10^8 and 23.165 respectively. The reduced mass used by Gribakin and Flambaum [2] is $1.211 \times 10^5 m_{\rm e}$ where $m_{\rm e}$ is the mass of an electron.

The characteristic lengths, γ_6, γ_8 and γ_{10} in bohr, are 203.1, 80.2 and 50.3 respectively. The semiclassical scattering length, $a_{\rm SC} = 68.061$ bohr found from expression (2), is remarkably accurate; a full quantum mechanical calculation yields the value $a = 68.216$ bohr.

In Table 2 we show the accumulated scattering lengths calculated quantum mechanically by the log-derivative implementation of the variable phase method [4,5] and calculated semiclassically by evaluating formula (21). We show in column 3 the quantal values, $\tilde{a}$, that were also checked by substituting the accumulated quantal values into equation (23). In equation (23) and later in evaluating the quadrature in equation (27) below we calculated the Bessel functions from their asymptotic forms for large argument, which contain higher order terms in the inverse of the argument than does equation (11), and from their power series expansions for small argument [3]. We show in column 6 the semiclassical values, $\tilde{a}_{\rm SC}$, that were obtained from equation (2) with the modified potential $\tilde{V}(R^*; R)$. Table 2 also displays the errors $\delta_1(R^*)$ and $\delta_2(R^*)$ defined by equations (14) and (16). The accumulated semiclassical and quantal scattering lengths agree well and the errors $\delta_1(R^*)$ and $\delta_2(R^*)$ are largely equal, leading to cancellation in equation (19), when $40 \le R^* \le 80$ (bohr),

Table 2. Scattering lengths and errors for ^{133}Cs-^{133}Cs (bohr).

	Quantal			Semiclassical		
R^*	Acc[a]	$\tilde{a}$[b]	Err[c]	Acc[d]	$\tilde{a}^{\rm b}_{\rm SC}$	Err[e]
40	38.49	103.4	–35.16	38.51	100.9	–32.86
50	52.22	80.12	–11.91	52.28	81.68	–13.62
55	50.95	78.72	–10.51	51.05	77.40	–9.34
60	76.91	73.91	–5.70	78.21	74.68	–6.62
70	66.87	72.16	–3.94	67.04	71.64	–3.58
80	49.81	70.50	–2.28	51.92	70.16	–2.10
90	151.3	69.21	–0.99	166.5	69.38	–1.31
100	118.9	68.92	–0.71	122.0	68.92	–0.86

[a] Accumulated length at R^*, quantal by variable phase method, equation (20).
[b] Scattering length for interaction $-C_6R^{-6}$ for $R > R^*$.
[c] Error $\delta_1(R^*)$ defined by equation (14).
[d] Accumulated length at R^*, semiclassical from equation (21).
[e] Error $\delta_2(R^*)$ defined by equation (16).

corresponding to $13.0 \geq x^* \geq 3.2$. The agreement between the errors deteriorates when R^* exceeds 80 bohr which is expected because then condition (7) or (8) is not satisfied so well; for example $3.2 \geq x^* \geq 2.1$ when $80 \leq R^* \leq 100$ (bohr).

2.5 Cancellation of errors

We need to consider whether or not the errors $\delta_1(R^*)$ and $\delta_2(R^*)$ tend to cancel in general. We can study the first order errors more generally. We show below that the first order errors do tend to cancel when x^* is large and condition (7) or (8) is satisfied.

First we establish an approximation to an integral involving the Bessel functions. Let us define

$$I_{i,j,n}(x) = \int_0^x J_{\frac{i}{4}}(s) s^n J_{\frac{j}{4}}(s) ds \tag{27}$$

where i and j take values ± 1. This function appears in equation (31) below for the first order error that arises from neglect of the higher order dispersion terms. We seek an estimate to this integral. It is plausible that it is dominated by the contributions from larger values of s because the integrand is weighted by s^2 or s^3 and the product $sJ_{-\frac{1}{4}}(s)$ is finite at $s = 0$. When x is sufficiently large that equations (11) provide good approximations to the Bessel functions we find from integration by parts that

$$I_{i,j,n}(x) \approx \frac{x^n 2^{-|i-j|/2}}{n\pi} \tag{28}$$

for $i = \pm 1$, $j = \pm 1$ and $n = 2, 3$; the error is $\mathcal{O}(x^{n-1})$. We show values of the integrals (27) obtained by numerical quadrature in Figures 1 and 2 in which the smooth dotted curves represent the approximate values defined by equation (28); as earlier we calculated the Bessel functions from their asymptotic forms for large argument and from their power series expansions for small argument [3]. It can be seen that the values of the integrals oscillate closely around the approximate values. We also illustrate

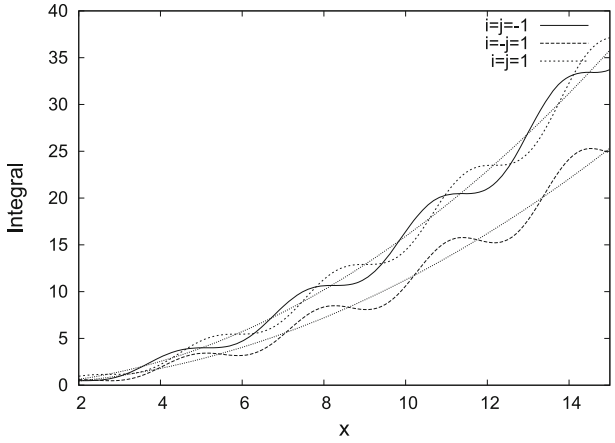

Fig. 1. Integral of equation (27) with $n = 2$.

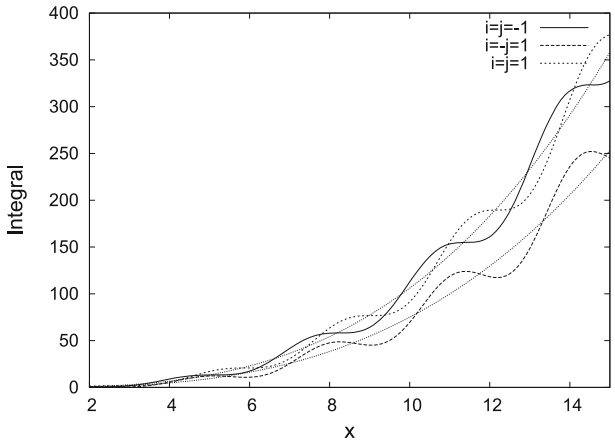

Fig. 2. Integral of equation (27) with $n = 3$.

the validity of the approximation of equation (28) in Table 3 where we show the ratio

$$\rho_{i,j,n}(x) = I_{i,j,n}(x) \div \frac{x^n 2^{-|i-j|/2}}{n\pi} \tag{29}$$

for a range of values of x.

The error $\delta_1(R^*)$ is given to first order in the neglected part, $-C_8/R^8 - C_{10}/R^{10}$, of the potential by [7]

$$\delta_1(R^*) = -\frac{2\mu}{\hbar^2} \int_{R^*}^{\infty} \phi(R) \left[\frac{C_8}{R^8} + \frac{C_{10}}{R^{10}}\right] \phi(R) dR \tag{30}$$

which, from equation (6), can be reduced to

$$\delta_1(R^*) = -\sum_{n=3}^{n=4} 2\pi \left(\frac{\gamma_{2n+2}}{\gamma_6}\right)^{2n} \overline{a}\; 2^{n-3} \times \left[I_{-1,-1,n}(x^*) - \frac{\sqrt{2}a}{\overline{a}} I_{-1,1,n}(x^*) + \frac{a^2}{2\overline{a}^2} I_{1,1,n}(x^*)\right]. \tag{31}$$

Equation (17) for $\delta_2(R^*)$ is exact. It contains the term $\sqrt{-2\mu V_{\rm L}(R)}$ with $V_{\rm L}(R)$ given by equation (1). By retaining only the terms that are linear in C_8 and C_{10} in

Table 3. Ratio $\rho_{i,j,n}(x)$ defined by equation (29).

i, j, n	$-1,-1, 2$	$-1, 1, 2$	$1,1,2$	$-1,-1,3$	$-1,1,3$	$1,1,3$
x			$\rho_{i,j,n}(x)$			
2	0.76	1.32	1.51	0.55	1.12	1.54
3	0.67	0.51	0.81	0.62	0.25	0.62
4	1.17	1.06	0.87	1.32	1.16	0.83
5	1.00	1.21	1.20	1.00	1.30	1.29
6	0.82	0.78	0.95	0.76	0.67	0.91
7	1.08	0.97	0.89	1.14	0.99	0.84
8	1.04	1.16	1.11	1.07	1.24	1.17
9	0.88	0.89	1.00	0.83	0.83	0.99
10	1.03	0.94	0.91	1.06	0.93	0.86
11	1.06	1.12	1.07	1.09	1.19	1.10
12	0.92	0.94	1.02	0.88	0.91	1.03
13	1.00	0.93	0.92	1.01	0.90	0.88
14	1.06	1.10	1.04	1.09	1.15	1.06
15	0.94	0.98	1.04	0.91	0.97	1.05

Table 4. First order corrections and corrected scattering lengths for ^{133}Cs-^{133}Cs (bohr).

	Quantal			Semiclassical		
R^*	Cor[a]	Cor[b]	a[c]	Cor[a]	Cor[b]	a^c_{SC}
40	–30.75	–1.98	70.67	–30.67	–1.97	68.26
50	–12.92	–0.53	66.66	–12.86	–0.53	68.29
55	–8.87	–0.30	69.55	–8.92	–0.30	68.18
60	–6.39	–0.18	67.33	–6.37	–0.18	68.13
70	–3.48	–0.07	68.61	–3.49	–0.07	68.08
80	–2.06	–0.03	68.41	–2.06	–0.03	68.07
90	–1.29	–0.02	68.90	–1.29	–0.02	67.07
100	–0.85	–0.01	68.06	–0.85	–0.01	68.06

[a] Correction proportional to C_8.
[b] Correction proportional to C_{10}.
[c] Corrected scattering length.

the binomial expansion of $\sqrt{-2\mu V_L(R)}$ we find that the error $\delta_2(R^*)$ is given to first order in the neglected part, $-C_8/R^8 - C_{10}/R^{10}$, of the potential by

$$\delta_2(R^*) = -\overline{a}\left(1-\frac{a}{\overline{a}}+\frac{a^2}{2\overline{a}^2}\right)\left[\left(\frac{\gamma_8}{\gamma_6}\right)^6 x^{*2}+\left(\frac{\gamma_{10}}{\gamma_6}\right)^8 \frac{4x^{*3}}{3}\right]. \quad (32)$$

From equation (28) and Table 3 we see that expressions (31) and (32) are almost equal, leading to cancellation in equation (19), when x^* is greater than around 6. The near equality (28) for the range of values of x^* that ensure that condition (7) or (8) is satisfied, but not necessarily that condition (12) or (13) is satisfied, is the main reason for the success of the semiclassical formula (2).

We illustrate the effect of the first order errors for the ^{133}Cs-^{133}Cs model problem in Table 4. In this table, columns 2 and 5 show the corrections that are proportional to C_8, columns 3 and 6 show the corrections that are proportional to C_{10} and columns 4 and 7 show the first order corrected scattering lengths. The uncorrected scattering lengths that were used are the values $\tilde{a}$ and $\tilde{a}_{SC}$ from Table 2.

3 Hybrid calculation

3.1 Method

In this method we combine the semiclassical method with a full numerical quantum mechanical calculation with long range corrections [4–6,8,9].

First we use semiclassical theory to calculate the accumulated scattering length at a chosen separation R^* that satisfies condition (7); we find this semiclassical accumulated scattering length $a_{SC}(R^*)$ from equation (21).

Secondly we make a quantum mechanical calculation by solving the variable phase equation (20) for $a(R)$ at separations $R \geq R^*$; this is a first order differential equation and therefore we need only one initial condition which we choose as $a(R^*) = a_{SC}(R^*)$. (Alternatively we could solve the zero energy wave equation by a suitable numerical propagator with a second initial condition obtained from a semiclassical calculation at a separation close to R^*.) Many of the oscillations of the zero energy wave function are accounted for by the semiclassical accumulated scattering length evaluated at separation R^*. The propagation of the accumulated scattering length from equation (20) (or the zero energy wave function) beyond R^* can be done with a much larger step than otherwise would be needed for an entire quantum mechanical calculation over the potential well. In our calculations we solved equation (20) by the log-derivative propagator [5].

Thirdly, after propagating the accumulated scattering length (or the zero energy wave function) to some large separation R_c we make the long range corrections at R_c [5,6,8,9].

The method of Clenshaw and Curtis [10] has been shown to be very effective in evaluating the quadratures that occur in semiclassical calculations [11]. We suggest its use for evaluating $a_{SC}(R^*)$ from equation (21).

3.2 Calculation for ^{7}Li-^{133}Cs

We show scattering lengths in Table 5 for ^{7}Li atoms interacting via the $X^1\Sigma^+$ potential with ^{133}Cs atoms. We used the potential of Staanum et al. [12] and took the mass of a ^{7}Li atom to be 7.016004 u and the mass of a ^{133}Cs atom to be 132.90544373 u [13]; with the mass of an electron, m_e, taken as $5.4857990943 \times 10^{-4}$ u the reduced mass is 12148.10 m_e with m_e taken as $5.4857990943 \times 10^{-4}$ u. The characteristic lengths, γ_6, γ_8 and γ_{10}, in bohr are 92.9, 44.5 and 30.7 respectively,

In Table 5 the quantal calculations of the accumulated scattering length were made by the log-derivative implementation of the variable phase method [4,5]. The semiclassical accumulated scattering lengths were obtained from formula (21). The hybrid calculations were made by propagating the scattering lengths, starting with the semiclassical values, by the log-derivative implementation of the variable phase method with long range corrections [4–6,8,9]. The switch from semiclassical quadrature to numerical propagation of the quantum mechanical wave equation in the hybrid method was made at R^*.

Table 5. Scattering lengths for ^{7}Li-^{133}Cs (bohr).

	$X^1\Sigma^+$			$a^3\Sigma^+$		
R^*	Acc[a]	Acc[b]	Hyb[c]	Acc[a]	Acc[b]	Hyb[c]
16	15.78	15.79	48.96	16.07	16.08	–1546
17	16.98	16.99	48.99	17.93	17.96	–1449
18	18.95	18.97	49.04	17.40	17.42	–1414
19	21.22	21.25	49.13	19.64	19.66	–1316
20	21.68	21.74	49.13	19.45	19.47	–1297
22	20.23	20.28	49.13	22.49	22.52	–1184
24	24.78	24.80	49.08	21.17	21.30	–1176
26	24.44	24.45	49.14	27.97	28.09	–1016

[a] Accumulated at R^*, quantal by variable phase method, equation (20).
[b] Accumulated at R^*, semiclassical from equation (21).
[c] Hybrid matched at R^*.

The semiclassical accumulated scattering length that was used in the hybrid method was evaluated by Clenshaw-Curtis quadrature with 300 pivots [10].

The semiclassical and quantal accumulated lengths agree well which is as expected because the values of x are relatively large. The complete semiclassical and quantal values and the hybrid value are in reasonably close agreement and with the values of Staanum et al. [12] (50 ± 20 bohr) and Du et al. [14] (50.5 bohr). The hybrid value fluctuates slightly as a function of R^* reflecting the differences between the quantal and semiclassical accumulated scattering lengths.

Near to a zero energy resonance there is considerable instability in the calculated scattering length and because the influence of errors then becomes magnified we do not expect agreement between semiclassical and quantal values. We see this in a calculation of scattering lengths for ^{7}Li atoms interacting via the $a^3\Sigma^+$ potential with ^{133}Cs atoms. We used the potential of Staanum et al. [12]. The values are −2809 bohr, quantal, and −1898 bohr, semiclassical. We show the accumulated and hybrid values in Table 5. Although the quantal and semiclassical values are quite close the hybrid value changes rapidly with R^*. This is a reflection of the ill-conditioned nature of this scattering length calculation. Du et al. [14] found a quantal value of −135.7 bohr calculated by the variable phase method. Staanum et al. [12] have noted that because of the extreme instability any calculated value is unreliable; they found that a change in the method for interpolating the potential from the tabulated ab initio values could change the sign of the $a^3\Sigma^+$ scattering length.

3.3 Calculation for H-H

The semiclassical formula fails completely for H-H collisions. For a pair of H atoms, each of mass 1.007276 u or 1836.153 m_e, interacting via the $X^1\Sigma_g^+$ Born Oppenheimer potential the quantal value of the scattering length is 0.5706 bohr and the semiclassical value is −2.781 bohr which not only has the wrong sign but has five times too great a magnitude. We illustrate the shortcomings of the semiclassical formula from calculations made by the hybrid method as follows. We used the Born Oppenheimer potential for numerical illustration only; the influences of the mass and of various corrections are significant [15–18] but do not change our conclusion. We constructed the potential from the Born Oppenheimer ab initio values of Wolniewicz et al. [19,20], the van der Waals coefficients of Yan et al. [21] and the exchange energy of Herring and Flicker [22]. The characteristic lengths are $\gamma_6 = 10.54$, $\gamma_8 = 7.82$ and $\gamma_{10} = 7.04$, all in bohr.

Table 6. Scattering lengths for H-H (bohr).

R^*	Acc[a]	Acc[b]	Hyb[c]
1.6	1.493	1.491	0.49
1.8	1.472	1.461	0.51
2.0	0.394	0.194	0.52
2.2	1.547	1.526	0.54
2.4	2.221	2.220	0.55
2.6	2.536	2.536	0.56
2.8	2.806	2.806	0.57
3.0	3.172	3.174	0.59
3.2	3.066	3.067	0.60
3.4	3.469	3.470	0.64
3.6	3.385	3.388	0.65

[a] Accumulated at R^*, quantal by variable phase method, equation (20).
[b] Accumulated at R^*, semiclassical from equation (21).
[c] Hybrid matched at R^*.

We show the quantal and semiclassical accumulated scattering lengths and the hybrid values in Table 6. It can be seen that over the well the quantal and semiclassical accumulated values are quite close confirming that even with this small reduced mass semiclassical theory gives a good account of the motion at these separations. The hybrid value varies slowly with the matching separation R^* and is close to the value from the full quantum mechanical calculation. This confirms that the main source of the error in the semiclassical formula lies in the treatment of the long range interaction; in this case the value of $R_{\max}$ is so small that the long range interaction cannot be accounted for by the first order corrections alone and that their cancellation is insufficiently precise. It can be seen that the difference between the quantal and semiclassical accumulated scattering lengths changes sign around 2.6 bohr; this reflects the minimum of the semiclassical potential error $\delta V(R)$ given by equation (10), which we found to occur at 2.41 bohr, and the point of inflection of the potential at 2.14 bohr.

In all the calculations described in Section 3 we evaluated the complete scattering lengths by the variable phase method and also, as a check, from the limit at zero energy of the s-wave phase shifts scaled by the wavenumber.

4 Conclusion

We have shown that the semiclassical expression for the scattering length contains two errors. We have shown, using an approximation for integrals of Bessel functions, that

the success of the semiclassical method is attributable to the near cancellation of these errors in first order. We have also demonstrated the cancellation of errors numerically.

We have described a hybrid method that combines advantages of the semiclassical approach with a quantum mechanical technique in an attempt to avoid the errors altogether. However we found the hybrid value can vary with the matching separation (where the calculation is changed from semiclassical to quantal) and therefore we suggest that the hybrid method is used only as a check on scattering lengths that have been calculated otherwise. We recommend that the semiclassical and hybrid methods are both used to check full quantum mechanical calculations because of the often ill-conditioned nature of scattering length calculations; full quantum mechanical calculations contain no intrinsic approximations. If all three methods produce values that are in reasonable agreement with one another then we gain confidence in the quantum mechanical calculation; if they differ, and the hybrid values show substantial variation with matching separation, then we are warned of ill-conditioning and we must endeavour to ensure that nothing in the quantal mechanical method, such as inadequate representation of the interaction potential, produces errors. The semiclassical and hybrid calculations can be made very rapidly with the aid of Clenshaw-Curtis quadrature [10].

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