Semiclassical approximation for the Scattering Volume in Cold-Atom Collisions

A S Dickinson
School of Natural Sciences (Physics), Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
E-mail: A.S.Dickinson@ncl.ac.uk

PACS numbers: 31.15.xg,34.50.Cx

Abstract. A semiclassical result is derived for the scattering volume for near-threshold $p$-wave scattering by a potential falling off as $1/R^n$, $n \geq 6$. $R$ being the interatomic separation. This result depends only on the $s$-wave zero-energy classical action and properties of the long-range potential and hence can be related to the semiclassical result for the scattering length. The exact result for the scattering volume for the Lennard-Jones $(2n-2,n)$, $n \geq 6$ is derived and it is shown that the corresponding semiclassical result is within 1% for potentials supporting at least two rotationless bound levels. Comparisons are made for the scattering volume with a variety of results in the literature for a range of systems supporting between 0 and 83 rotationless bound levels. The semiclassical result is generally within 5% and was never in error by more than 15%, which occurred for a case supporting no bound states.

30 July 2008
1. Introduction

The interactions of cold atoms are critical for determining their properties, such as the stability of Bose-Einstein Condensates (BEC), the formation of Degenerate Fermi Gases (DFG) and sympathetic cooling rates. For temperatures so low that only a few partial waves need be considered, near-threshold quantum reflection by long-range attractive potentials has been studied by Friedrich and collaborators (Friedrich and Trost, 2004, 2007). To determine the $s$-wave scattering length, however, short-range information is also required. Gribakin and Flambaum (1993) derived a semiclassical approximation to the scattering length using simple properties of the long-range potential and the zero-energy $s$-wave classical action, $A$. Later Flambaum et al. (1999) showed that the semiclassical effective range could also be expressed in terms of these quantities, thus providing an approximate relationship between the scattering length and the effective range. Using a form of quantum-defect theory for the inverse sixth-power potential Gao (1998) has also established a relation between the scattering length and the effective range. While he also discusses low energy $p$-wave scattering, he does not establish a connection between the $s$-wave and $p$-wave parameters. For the related problem of finding the binding energy of near-dissociation rovibrational levels Le Roy and Bernstein (1970) had shown that these energies could also be calculated from the same properties.

Particularly for sympathetic cooling, (Nguyen et al., 2005, and references therein) when the temperatures of interest have not quite reached the BEC or DFG regimes, it is useful to have available the near-threshold behaviour of the higher phase shifts (Ouerdane and Jamieson, 2004). For the most important case of the van der Waals dispersion interaction, falling off as $1/R^6$, for partial waves higher than $p$ the effective-range theory result is identical with the Born approximation for the long-range potential (Levy and Keller, 1963). However, for the $p$-wave, the low energy phase shift, $\delta_1(k) \approx -k^3V$, where $k$ denotes the wavenumber and the $V$ the scattering volume. The scattering volume is also employed in nuclear physics, see e.g. Stricker et al. (1979). The cube root of the scattering volume is sometimes referred to as a ‘scattering length’ (Brueckner, 1952) or as the $p$-wave scattering length (Bohn, 2000; Suno et al., 2003), although Szmytkowski (1995) uses this term for $V/3$. It can be anticipated that the scattering volume should also depend on the short-range interaction only through the value of the zero-energy action, $A$, and hence be expressible, like the effective range, (Flambaum et al., 1999), in terms of the scattering length. In this paper we derive such a relation and test it against the new exact result for a Lennard-Jones $(2n - 2, n)$ potential and for some literature values for the scattering volume.

In section 2 we derive the semiclassical result for the scattering volume. The quantal result for this for the Lennard-Jones $(2n - 2, n)$ potential is derived in section 3 and its relation to the the semiclassical result for this potential is established. Comparisons with literature values of the scattering volume are made for a variety of atom-atom potentials. A summary and conclusions are presented in section 4.
2. Semiclassical Theory

2.1. The Long-Range Solution.

We consider first only the attractive long-range potential \( V_0(R) = -C_n/R^{n} \), where \( R \) is the internuclear separation. We follow Friedrich and Trost (2004) and introduce the distance

\[
\beta_n = \left(\frac{2\mu C_n}{\hbar^2}\right)^{1/(n-2)},
\]

where \( \mu \) denotes the reduced mass. In terms of \( \beta_n \) the zero-energy Schrödinger equation can be written

\[
\frac{d^2}{dR^2} u_\ell(R) + \left[ \frac{-\ell(\ell+1)}{R^2} + \frac{\beta_n^{-2}}{R^n} \right] u_\ell(R) = 0,
\]

with general solution

\[
u = \frac{2\ell + 1}{n-2},
\]

assuming \( 2\ell < (n - 3) \) as otherwise different terms will be dominant in the expansion. Specializing to the case of interest, \( \ell = 1 \), giving \( \nu = 3/(n - 2) \),

\[
\lim_{R \to \infty} u_1(R) = \beta_n^{1/2} \left\{ \frac{K_1}{(n-2)^{\nu}} \frac{1}{\Gamma(1+\nu)} \left( \frac{\beta_n}{R} \right)^{\ell} + \frac{K_2(n-2)^{\nu}}{\Gamma(1-\nu)} \left( \frac{R}{\beta_n} \right)^{(\ell+1)} \right\}
\]

\[
= \frac{K_2(n-2)^{\nu}}{\Gamma(1-\nu) \beta_n^{(\ell+1)/2}} \left\{ R^{\ell+1} + \frac{K_1}{K_2(n-2)^{2\nu} \Gamma(1+\nu)} \frac{1}{R^2} \right\},
\]

where \( K_1 \) is a constant and \( V \) is the scattering volume, (Gutiérrez et al., 1984, eq.(7)), (Ouerdane and Jamieson, 2004, eq.(23)). From eq. (5) \( V \) is given by

\[
V = -\frac{K_1}{K_2} \frac{\beta_n^{3\nu} \frac{(n-3)}{(n-2)}}{3(n-2)^{6/(n-2)} \Gamma \left( \frac{n+1}{n-2} \right)}.
\]
Next consider the small $R$, large $\rho$, behaviour of $u_\ell(R)$:

$$\lim_{R \to 0} u_\ell(R) = R^{1/2} \sqrt{\frac{2}{\pi \rho}} \left[ K_1 \cos(\rho - \pi \nu/2 - \pi/4) + K_2 \cos(\rho + \pi \nu/2 - \pi/4) \right]$$

$$= \beta_{n}^{1/2} \sqrt{\frac{n-2}{\pi}} \left( \frac{R}{\beta_{n}} \right)^{n/4}$$

$$\times \left\{ \left[ K_1 + K_2 \cos \left( \frac{\pi(2\ell+1)}{n-2} \right) \right] \cos \theta_\ell(R) - K_2 \sin \left( \frac{\pi(2\ell+1)}{n-2} \right) \sin \theta_\ell(R) \right\}, \quad (7)$$

$$\theta_\ell(R) = \frac{2}{n-2} \left( \frac{\beta_{n}}{R} \right)^{(n-2)/2} - \frac{(2\ell+1)\pi}{2(n-2)} - \frac{\pi}{4}. \quad (8)$$

### 2.2. The Short-Range Solution

We wish to join this to the standard WKB solution, $w_\ell(R)$, regular at the origin, with the full potential and using the Langer correction (Child, 1991). For the attractive potentials of interest here the inner zero-energy classical turning point, $R_-$, of the effective potential will be close to the point where the potential crosses the axis. With the centrifugal potential present the outer zero-energy turning point, $R_+$, is finite, being on the inner side of the centrifugal barrier. Then

$$w_\ell(R) = p^{-1/2}(R) \cos [\Phi_\ell(R) - \pi/4], \quad R_- < R < R_+, \quad (9)$$

where $p(R)$ is the momentum at $R$ and

$$\Phi_\ell(R) = \int_{R_-}^{R} \sqrt{-\frac{2\mu V}{\hbar^2} - \frac{(\ell + 1/2)^2}{R^2}} \, dR$$

$$= \int_{R_-}^{R_+} \sqrt{-\frac{2\mu V}{\hbar^2} - \frac{(\ell + 1/2)^2}{R^2}} \, dR - \int_{R}^{R_+} \sqrt{\frac{\beta_{n}^{n-2}}{R^n} - \frac{(\ell + 1/2)^2}{R^2}} \, dR$$

$$\equiv A_\ell - I(R), \quad (10)$$

where $R$ is chosen sufficiently large that the potential can be well described by its asymptotic form, $V_0(R)$. For the $p$-wave solution $R_+ \approx \beta_{n}$ and $\beta_{n} \gg a_0$, because of the reduced mass dependence, see eq. (1), so this condition can be satisfied (see also the discussion of this in Gribakin and Flambaum (1993)). Evaluating $I(R)$ we obtain

$$I(R) = \frac{2}{n-2} \left\{ \sqrt{\left( \frac{\beta_{n}}{R} \right)^{n-2} - (\ell + 1/2)^2 - \frac{(\ell + 1/2)^2}{2}} \right\}$$

$$+ (\ell + 1/2) \arcsin \left[ (\ell + 1/2) \left( \frac{R}{\beta_{n}} \right)^{(n-2)/2} \right]$$

$$\approx \frac{2}{n-2} \left( \frac{\beta_{n}}{R} \right)^{(n-2)/2} - (\ell + 1/2)^2/2 \equiv \theta_\ell(R) + \pi/4, \quad (11)$$
Semiclassical approximation for the Scattering Volume

for \( R \ll R_+ \), using eq. (8). Hence

\[ \Phi_\ell(R) = A_\ell - \theta_\ell(R) - \pi/4. \]  

(12)

Thus we can write, from eq. (9),

\[ w_\ell(R) = p^{-1/2} \left[ \sin A_\ell \cos \theta_\ell(R) - \cos A_\ell \sin \theta_\ell(R) \right]. \]  

(13)

Comparing eqs. (7) and (13) we obtain

\[ \frac{K_1}{K_2} = -\cos \left( \frac{\pi(2\ell + 1)}{n - 2} \right) \left[ 1 - \tan \left( \frac{\pi(2\ell + 1)}{n - 2} \right) \tan A_\ell \right], \]  

(14)

thus relating \( K_1/K_2 \) to the short-range behaviour of the wavefunction through the value of \( A_\ell \).

2.3. The Semiclassical Scattering Volume

Using this result, eq. (14), with \( \ell = 1 \), in eq. (6),

\[ \mathcal{V}^{SC} = -\frac{\beta_6^3}{3(n - 2)^6} \frac{\Gamma(n-2)}{\Gamma(n+1)} \cos \left( \frac{3\pi}{n - 2} \right) \left[ 1 - \tan \left( \frac{3\pi}{n - 2} \right) \tan A_1 \right], \]  

(15)

where \( \mathcal{V}^{SC} \) denotes the semiclassical approximation to \( \mathcal{V} \). For the case of particular interest, \( n = 6 \), we have

\[ \mathcal{V}^{SC} = -\frac{\beta_6^3}{24\sqrt{2}\Gamma(7/4)} (1 + \tan A_1). \]  

(16)

From Dickinson and Bernstein (1970) we have

\[ A_\ell \approx A - \frac{\pi(2\ell + 1)}{2(n - 2)} \Rightarrow A_1 = A - 3\pi/8, \]  

(17)

for \( n = 6 \), where \( A \) is the zero-energy \( s \)-wave classical action, in units of \( \hbar \):

\[ A = (1/\hbar) \int_{R_-}^{\infty} \sqrt{-2\mu V(R)} \, dR. \]

Then

\[ \mathcal{V}^{SC} = -\frac{\beta_6^3}{24\sqrt{2}\Gamma(7/4)} [1 + \tan(A - 3\pi/8)]. \]  

(18)

Following the argument of Gribakin and Flambaum (1993, p 549) we see that for large and essentially random values of \( A \) the sign of \( \mathcal{V}^{SC} \) has the opposite behaviour to that of the sign of the scattering length, in that 75% of the values of \( A \) will give negative values of the scattering volume and the remainder positive values. The quantal values calculated by Ouerdane and Jamieson (2004) are consistent with these ratios, with 13 negative
values of $V$ in a sample of 18 calculations, see Tables 1 and 2. For the calculations of Gutiérrez et al. (1984) all six values were negative, see Table 3.

For a zero-energy $p$-wave bound state we have the condition

$$A - 3\pi/8 = (n + 1/2)\pi,$$  \hspace{1cm} (19)

where $n$ is a non-negative integer. Thus the critical value of $A$ just supporting $N$ $p$-wave bound states is larger by $\pi/4$ than the critical value for $N$ $s$-wave bound states.

Relating the expression for $V_{SC}$ in eq. (18) to the semiclassical expression for the $s$-wave scattering length, $a_{SC}$, (Gribakin and Flambaum, 1993):

$$a_{SC} = \bar{a} \left[ 1 - \tan(A - \pi/8) \right], \quad \bar{a} = \sqrt{2} \frac{\beta_6 \Gamma(3/4)}{\Gamma(1/4)},$$  \hspace{1cm} (20)

we find

$$V_{SC} = -\frac{\beta_6^3 \Gamma(1/4)}{12\sqrt{2} \Gamma(7/4)} \frac{\bar{a} - a_{SC}^{SC}}{2\bar{a} - a_{SC}^{SC}} \equiv -0.23246 \frac{\beta_6^3 \bar{a} - a_{SC}^{SC}}{2\bar{a} - a_{SC}^{SC}}.$$  \hspace{1cm} (21)

The value of the scattering volume $V$ going to infinity corresponds to a $p$-wave zero-energy bound state, so that, from eq. (21), $a_{SC}^{SC} = 2\bar{a}$. This now gives, from eq. (20), $\tan(A - \pi/8) = -1$, consistent with the condition eq. (19) obtained directly.

3. Results

3.1. Lennard-Jones ($2n-2,n$) Potentials

It has long been known (Dickinson and Bernstein, 1970, and references therein) that for all values of the angular momentum quantum number the zero-energy Schrödinger equation for the Lennard-Jones (LJ) ($2n-2,n$) potential can be solved in terms of the standard functions of analysis. This result has also been rederived recently (Gao, 2003, 2004; Pade, 2007). Using this solution Gao and Pade have obtained the exact result for the scattering length for this potential. We define the LJ ($2n-2,n$) potential as

$$V(R) = \frac{\hbar^2}{2\mu R^2} \left[ \left( \frac{\beta_{2n-2}}{R} \right)^{2n-4} - \left( \frac{\beta_n}{R} \right)^{n-2} \right].$$  \hspace{1cm} (22)

The radial wavefunction regular at the origin is given for $\ell < 2$ (Pade, 2007, eq.(6)) in terms of the Kummer function $U(\alpha, \beta, z)$ (Abramowitz and Stegun, 1965) but with the parameters $\alpha$ and $\beta$, in the notation of Pade (2007), given by

$$\alpha = \frac{2\ell + n - 1 - r_0 \sqrt{u}}{n - 2}, \quad \beta = \frac{2\ell + n - 1}{n - 2}.$$  \hspace{1cm} (23)

Then

$$V = \frac{\beta_6^3}{3} \left( \frac{2}{n - 2} \right)^{n-2} \left( \frac{\beta_{2n-2}}{\beta_n} \right)^3 \frac{\Gamma \left( \frac{n+1}{2(n-2)} - A/\pi \right) \Gamma \left( \frac{n-5}{n-2} \right)}{\Gamma \left( \frac{n-5}{2(n-2)} - A/\pi \right) \Gamma \left( \frac{n+1}{n-2} \right)}, \quad n \geq 6,$$  \hspace{1cm} (24)
where

\[ A = \frac{\pi}{2(n - 2)} \left( \frac{\beta_n}{\beta_{2n-2}} \right)^{n-2} \] (25)

is the classical action, in units of ħ, for this potential. Using this result for \( A \) in eq. (15) and using eq. (17) we obtain

\[ V^{SC} = \frac{\beta_n^3}{3(n - 2)^{6(n-2)/n}} \frac{\Gamma \left( \frac{n-5}{n-2} \right)}{\Gamma \left( \frac{n-1}{n-2} \right)} \cos \left( \frac{3\pi}{n} \right) \left\{ 1 - \tan \left( \frac{3\pi}{n-2} \right) \tan \left[ A - \frac{3\pi}{2(n-2)} \right] \right\} \] (26)

To relate the exact result, eq. (24), to this semiclassical result we use the reflection formula for Γ functions and then use an approximation from Abramowitz and Stegun (1965, ch. 6) for the ratio of Gamma functions of large argument:

\[
\frac{\Gamma \left( \frac{n+1}{2(n-2)} - A/\pi \right)}{\Gamma \left( \frac{n-5}{2(n-2)} - A/\pi \right)} \approx \frac{\cos \left( \frac{A + \frac{3\pi}{2(n-2)}}{\pi} \right)^{3/(n-2)} \left\{ 1 + O \left( \frac{\pi}{A} \right)^2 \right\}}{\cos \left( \frac{A - \frac{3\pi}{2(n-2)}}{\pi} \right)^{3/(n-2)} \left\{ 1 - \tan \left( \frac{3\pi}{n} \right) \tan \left[ A - \frac{3\pi}{2(n-2)} \right] \right\}}.
\] (27)

This approximation is surprisingly accurate: when \( n = 6 \) for \( A = 1.25\pi \) the error in the ratio of Γ functions is below 1% and by \( A = 10\pi \) the error is down to 0.01%. Comparable accuracy was noted by Pade (2007) in the analogous approximation for the scattering length.

Using eq. (27) in eq. (24) the semiclassical result, eq. (26), is regained.

### 3.2. Comparison with Numerical Results

Ouerdane and Jamieson (2004) have calculated values for the scattering length and scattering volume for four isotopomers of LiRb and for up to three potentials and two isotopomers for \( ^{23}NaRb \). Since it is difficult to reproduce precisely all the details of the potentials employed in these calculations we test the semiclassical expression for \( V \) by employing the calculated quantal value for the scattering length, \( a \), in eq. (21) to estimate the value of \( V^{SC} \). These systems support between 15 and 83 s-wave bound levels (Ouerdane and Jamieson, 2004).

Results are shown in Tables 1 and 2. The majority of the results for \( V^{SC} \) shown in these tables are within 5% of the quantal values, with the largest difference being about 10%. The two biggest differences occur for examples in the \( a^3\Sigma^+ \) potential of NaRb where \( a \approx 2 \tilde{a} \). As discussed in section 2.3, this is close to the condition for a zero-energy bound state and then the value of \( V^{SC} \) is particularly sensitive to the value of the classical action and hence to the value of \( a \). For \( ^{23}Na^{85}Rb \) with potential \( d \), see
Table 1. Comparison of results from eq. (21) with quantal results for various isotopomers and potentials for $^{23}$NaRb.

<table>
<thead>
<tr>
<th>Potential</th>
<th>$X^1\Sigma^+ 85\text{Rb}$</th>
<th>$X^1\Sigma^+ 87\text{Rb}$</th>
<th>$a^3\Sigma^+ 85\text{Rb}$</th>
<th>$a^3\Sigma^+ 87\text{Rb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^e (a_0)$</td>
<td>174</td>
<td>62</td>
<td>178</td>
<td>84</td>
</tr>
<tr>
<td>$V^e (10^3 a_0^3)$</td>
<td>-682</td>
<td>52.8</td>
<td>-663</td>
<td>373</td>
</tr>
<tr>
<td>$V^{SC} (10^3 a_0^3)$</td>
<td>-665</td>
<td>50.8</td>
<td>-647</td>
<td>391</td>
</tr>
</tbody>
</table>

a Using potential of Docenko et al. (2004). [We follow the labelling of the potentials employed by Ouerdane and Jamieson (2004).]
b Using potential of Korek et al. (2000).
e From Ouerdane and Jamieson (2004).

Table 2. Comparison of results from eq. (21) with quantal results for various isotopomers of LiRb. The notation $n_1-n_2$ denotes $^{n_1}\text{Li}^{n_2}\text{Rb}$.

<table>
<thead>
<tr>
<th></th>
<th>$X^1\Sigma^+$</th>
<th>$a^3\Sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6-85$</td>
<td>$6-87$</td>
<td>$7-85$</td>
</tr>
<tr>
<td>$a^e (a_0)$</td>
<td>-40</td>
<td>-64</td>
</tr>
<tr>
<td>$V^e (10^3 a_0^3)$</td>
<td>-97.7</td>
<td>-105.9</td>
</tr>
<tr>
<td>$V^{SC} (10^3 a_0^3)$</td>
<td>-94.8</td>
<td>-102.8</td>
</tr>
</tbody>
</table>
e From Ouerdane and Jamieson (2004).

Table 3. Comparison of results from eq. (21) with quantal results for $\text{H}_2$, $\text{D}_2$, and $^{3,4}\text{He}_2$.

<table>
<thead>
<tr>
<th></th>
<th>$^{3}\text{He}$</th>
<th>$^{4}\text{He}$</th>
<th>$^{3}\text{He}$</th>
<th>$^{4}\text{He}$</th>
<th>$^{3}\text{He}$</th>
<th>$^{4}\text{He}$</th>
<th>$\text{H}_2/\text{D}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^c (\text{Å})$</td>
<td>-6.97</td>
<td>125.1</td>
<td>-6.1</td>
<td>-176.3</td>
<td>59.8</td>
<td>0.709</td>
<td>-3.63</td>
</tr>
<tr>
<td>$V^e (\text{Å}^2)$</td>
<td>-26.1</td>
<td>-42.1</td>
<td>-26.2</td>
<td>-41.2</td>
<td>-14.8$\times$10$^3 c$</td>
<td>-19.6</td>
<td>-50.6</td>
</tr>
<tr>
<td>$V^{SC} (\text{Å}^2)$</td>
<td>-23.3</td>
<td>-36.9</td>
<td>-24.8</td>
<td>-39.0</td>
<td>-15.3$\times$10$^3 c$</td>
<td>-16.6</td>
<td>-45.1</td>
</tr>
</tbody>
</table>
a Aziz et al. (1979).
b de Boer and Michels (1938).
c Dickinson et al. (2004), results for the $1^5\Sigma^+_g$ potential.
e From Gutiérrez et al. (1984).

Table 1, a change of $\pm 0.5 a_0$ in the value of $a$ leads to a change of about 10% in the value of $V^{SC}$.

For particularly unfavourable cases for semiclassical methods we consider the results obtained for $a$ and $V$ by Gutiérrez et al. (1984) for $^4\text{He}$ and $^3\text{He}$ scattering on both the potential of Aziz et al. (1979) and the early Lennard-Jones (12,6) potential of de Boer and Michels (1938), and for $\text{H}$–$\text{H}$ and $\text{D}$–$\text{D}$ scattering on the $b^3\Sigma^+_u$ potential of Kolos and Wolniewicz (1974). Of these six cases, only for $^4\text{He}$ on the potential of Aziz et al. (1979) is an $s$-wave bound state supported. Comparisons presented in Table 3 show that the worst case is for hydrogen scattering where the discrepancy is 15%.
We have also included in this table results for metastable Helium scattering on the $1^5Σ^+_g$ potential, which supports 13 bound levels for $^3$He collisions (Dickinson et al., 2004). In this case the value of $V^{SC}$ has been determined using the semiclassical value for $a$, equivalent to using the value of $A$ directly in eq. (18). Note that the sign of $V$ in Dickinson et al. (2004) was reversed.

4. Summary and Conclusions

A semiclassical result has been derived for the scattering volume for $p$-wave scattering with long-range potentials falling off at least as fast as $1/R^6$. This result has considerable similarities with the corresponding semiclassical result for the scattering length (Gribakin and Flambaum, 1993). Like that result, the scattering volume can be expressed in terms of the $s$-wave zero-energy classical action and the leading coefficient of the long-range behaviour of the potential. Hence, as for the effective range (Flambaum et al., 1999), the scattering volume can be expressed in terms of the scattering length and long-range properties. This opens up the possibility of estimating the scattering volume once the scattering length is available, either from scattering or from the binding energy of the highest rotationless level.

The quantal scattering volume has been derived for the Lennard-Jones $(2n − 2, n)$, $n \geq 6$, potential and it was shown that in the limit of large values of the classical action this quantal result reduces to the corresponding semiclassical result. In practice, values of the classical action large enough to support even two rotationless bound states give semiclassical results within a percent of the exact result.

Comparison was made with a number of literature values for a range of potentials and the accuracy of the semiclassical result was generally within 5% of the quantal result. Even for a potential too weak to support a bound state the discrepancy was only 15%.

Overall these comparisons suggest that the semiclassical result for the scattering volume can provide a robust estimate of the full result, once the scattering length and the long-range properties are known.

References


REFERENCES