Analytical calculation of cold-atom scattering

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The interaction between atoms behaves as $-\alpha/r^n$ at large distances and, owing to the large reduced mass μ of the collision pair, allows a semiclassical treatment within the potential well. As a result, the low-energy scattering is governed by two large parameters: the asymptotic parameter $\gamma = \sqrt{2\mu\alpha}/\hbar \gg a_0^{(n-2)/2}$ (a_0 is the Bohr radius) and the semiclassical zero-energy phase $\Phi \gg 1$. In our previous work [Phys. Rev. A **48**, 546 (1993)] we obtained an analytical expression for the scattering length a, which showed that it has 75% preference for positive values for $n=6$, characteristic of collisions between ground-state neutral atoms. In this paper we calculate the effective range and show that it is a function of a, $r_e = F_n - G_n/a + H_n/a^2$, where F_n, G_n, and H_n depend only on γ. Thus, we know the s-phase shift at low momenta $k \ll \gamma^{-2/(n-2)}$ from the expansion $k \cot \delta_0 \simeq -1/a + \frac{1}{2} r_e k^2$. At $k \gg \gamma^{-2/(n-2)}$ the phase shift is obtained semiclassically as $\delta_0 = \Phi + \pi/4 - I_n \gamma^{2/n} k^{(n-2)/n}$, where $I_n = [n/(n-2)]\Gamma((n-1)/n)\Gamma((n+2)/2n)/\sqrt{\pi}$. Therefore, γ and Φ determine the s-wave atomic scattering in a wide range of momenta, as well as the positions of upper bound states of the diatomic molecule. [S1050-2947(99)03603-3]

I. INTRODUCTION

The character of the interaction between atoms in very-low-energy collisions is determined by the sign and magnitude of the atom-atom scattering length a. Negative a mean attraction, and positive a correspond to repulsion between the atoms. The value of a is crucial for the properties of atomic gases at very low temperatures. In particular, for bosonic atoms with $a>0$ the possible Bose condensate is stable, whereas for $a<0$ it is unstable, and only a finite number of atoms can be found in the condensate state in a trap. Large absolute values of a describe situations when a virtual ($a<0$) or a weakly bound ($a>0$) level exists for the atomic pair. In the latter case the energy of this level can be estimated as $E = -\hbar^2 \kappa^2/2\mu$ (μ is the reduced mass of the atoms), where $\kappa = 1/a$. A more accurate estimate can be obtained by taking into account the next term in the low-energy expansion of the s-wave phase shift δ_0,

$$k \cot \delta_0 \simeq -\frac{1}{a} + \frac{1}{2} r_e k^2, \qquad (1)$$

and using

$$\kappa = \frac{1}{a} + \frac{1}{2} r_e \kappa^2 \qquad (2)$$

to find the weakly bound energy level, where r_e is the so-called effective range [1].

If the interatomic potential is known to sufficiently high accuracy, all bound-state and scattering properties can be obtained by numerical integration of the second-order (Schrödinger) equation. However, in many cases the errors in the calculated potential curves do not allow one to determine even the sign of the scattering length or the total number of bound states. The potential curve can be refined if some experimental data on the positions of the bound states or photoassociation intensities are available. To make this process

effective one needs to know what the main characteristics of the interatomic potential are that one has to tune to obtain accurate results, in other words, what the quantities are that the observed effects are most sensitive to. At this point an analytical approach would be most useful in providing guidance and uncovering some important physics of the low-energy atom-atom scattering.

There are two features of the interaction between the atoms that allow one to tackle this problem analytically. First, the potential at large distances behaves as an inverse power of the interatomic distance,

$$U(r) \simeq -\frac{\alpha}{r^n}, \qquad (3)$$

with $n=6$ for spherically symmetric neutral atoms. The asymptotic parameter $\alpha \equiv C_6$ is known quite well for most atomic pairs of interest. Second, for atoms other than hydrogen and helium the potential curve is usually quite deep, even when the electron-exchange part of the atomic interaction is repulsive, as for ${}^3\Sigma_u$ terms of alkali-metal atoms. ''Deep'' here means that the wave function of the atomic pair oscillates many times within the potential well, even at very low collision energies, and accordingly, the interatomic potential supports a large number of vibrational levels. This latter property enables one to use the semiclassical (or WKB) approximation to describe the motion of atoms within the potential well.

Based on these two properties a formula for the scattering length was obtained in our previous work [2],

$$a = \bar{a}\left[1 - \tan\left(\frac{\pi}{n-2}\right)\tan\left(\Phi - \frac{\pi}{2(n-2)}\right)\right], \qquad (4)$$

where $\bar{a}$ is the *mean* or ''typical'' scattering length determined by the asymptotic behavior of the potential through the parameter $\gamma = \sqrt{2\mu\alpha}/\hbar$,

$$\bar{a}=\cos\left(\frac{\pi}{n-2}\right)\left(\frac{\gamma}{n-2}\right)^{2/(n-2)}\frac{\Gamma\left(\frac{n-3}{n-2}\right)}{\Gamma\left(\frac{n-1}{n-2}\right)}, \tag{5}$$

and Φ is the semiclassical phase calculated at zero energy from classical turning point r_0 where $U(r_0)=0$, to infinity,

$$\Phi=\int_{r_0}^{\infty}\sqrt{-2mU(r)}\,dr. \tag{6}$$

It also determines the total number of vibrational levels with zero orbital angular momentum [2],

$$N_s=\left[\frac{\Phi}{\pi}-\frac{n-1}{2(n-2)}\right]+1, \tag{7}$$

where [ ] is the integer part. When the difference in brackets is just below an integer the scattering length Eq. (4) is anomalously large negative, $|a|\gg\bar{a}$, which corresponds to the presence of a virtual level at $E=\hbar^2/2\mu a^2$, and when it exceeds an integer by a margin, a is very large positive, due to the existence of a weakly bound state. Unlike γ and $\bar{a}$ the phase factor Φ depends strongly on the actual shape of the interatomic potential well. When the phase is large, $\Phi/\pi\gg1$, the scattering length is very sensitive to the slightest changes of the potential. The error can be estimated by using Eq. (6).

When the potential is not known to sufficient accuracy, i.e., when the error in the phase is $\delta\Phi\sim1$, one can still use Eqs. (4) and (5) to estimate the typical scattering length values that one can expect for a given mass and van der Waals constant C_6. For most atomic pairs the value of $\gamma=\sqrt{2\mu C_6}$ (in atomic units) is much larger than unity, e.g., $\gamma=4.2\times10^3$, 7.9×10^3, 2.7×10^4, and 4.1×10^4 for Li, Na, Rb, and Cs, respectively, and the corresponding scattering lengths $a\sim\bar{a}\approx0.478\sqrt{\gamma}$ are *parametrically* large. Equation (4) also shows that for potentials $U(r)\propto1/r^6$ there is a 3:1 preference for positive values of a. This means that for about 75% of atomic pairs the scattering lengths are positive, and, consequently, the corresponding Bose condensates would be stable.

In this work we calculate the effective range in atomic collisions analytically and show that it is a simple function of γ and a (and, consequently, Φ); see Eq. (24). We calculate the values of r_e for various collision states of Li$_2$, Na$_2$, and Cs$_2$ by using the scattering lengths obtained numerically by other authors [3–5], and demonstrate that our analytical formula for r_e is exceptionally accurate. Its results agree with the direct numerical r_e to better than 1%.

From a more general point of view this result is part of a "theorem" that states that for deep potentials with asymptotic behavior (3) the scattering phase shift is determined by γ and Φ alone, as long as the scattering energy is much smaller than the depth of the potential well. This theorem follows from the fact that at smaller distances where the potential is deep it can be replaced by an energy-independent boundary condition. We illustrate this statement by calculating the s-phase shift semiclassically at $k\bar{a}\gg1$, where it has a simple explicit dependence on Φ and γ.

II. CALCULATION OF THE EFFECTIVE RANGE

The effective range r_e in Eq. (1) can be found from the integral [6]

$$r_e=2\int_0^{\infty}[\chi_0^2(r)-\chi^2(r)]dr, \tag{8}$$

where $\chi(r)$ is the solution of the radial Schrödinger equation for the s partial wave at zero energy,

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{dr^2}+U(r)\chi(r)=0, \tag{9}$$

with the boundary condition $\chi(0)=0$, normalized at $r\to\infty$ as

$$\chi(r)\simeq1-\frac{r}{a}, \tag{10}$$

where a is the scattering length and χ_0 is the zero-energy solution of the Schrödinger equation for the free motion $[U(r)=0]$, equal to the asymptotic form (10) everywhere: $\chi_0(r)=1-r/a$. The integral in Eq. (8) converges provided χ approaches χ_0 rapidly enough as $r\to\infty$. This requires $U(r)$ to decrease faster than r^{-5}.

At large distances the potential is given by Eq. (3) and Eq. (9) has an analytical solution in terms of the Bessel functions $J_{1/(n-2)}$ and $N_{1/(n-2)}$ [1] (see below). This potential also satisfies the condition for the validity of the semiclassical approximation

$$\frac{m\hbar|F|}{p^3}\ll1, \tag{11}$$

where $F=-dU/dr$ and $p=\sqrt{2\mu[E-U(r)]}$, at

$$r\ll\left(\frac{2\gamma}{n}\right)^{2/(n-2)}, \tag{12}$$

for $E=0$. For interatomic potentials the above boundary is usually much greater than the atomic radii. For example, inequality (12) reads as $r\ll117$ a.u. for Cs, $r\ll51.2$ a.u. for Na, and $r\ll37.5$ for Li. At small distances $U(r)$ does not have the simple form of Eq. (3); however, the semiclassical approximation remains valid there. Hence, there is always a range of distances r^* satisfying Eq. (12) where both the semiclassical approximation and the analytical solution of Eq. (9) with $U(r)=-\alpha/r^n$ are valid. As a result, one can present the wave function at $E=0$ explicitly as [2]

$$\chi(r)=\frac{C}{\sqrt{p}}\sin\left(\frac{1}{\hbar}\int_{r_0}^r p\,dr+\frac{\pi}{4}\right),\quad r_0<r\lesssim r^*, \tag{13}$$

$$\chi(r)=\sqrt{r}\left[AJ_{1/(n-2)}\left(\frac{2\gamma}{n-2}r^{-(n-2)/2}\right)\right.$$
$$\left.-BN_{1/(n-2)}\left(\frac{2\gamma}{n-2}r^{-(n-2)/2}\right)\right],\quad r^*\lesssim r<\infty, \tag{14}$$

where r_0 is the classical turning point and $p=\sqrt{-2mU(r)}$ is the classical momentum. To the left of r_0 the wave function $\chi(r)$ decreases exponentially.

By matching χ and $d\chi/dr$ from Eqs. (13) and (14) at r^*, and comparing the asymptotic form of Eq. (14) at $r\to\infty$ with Eq. (10), we obtain the scattering length a, Eq. (4), and the constants A, B, and C in terms of γ and the semiclassical phase Φ, Eq. (6):

$$B = -\frac{1}{a}\sin\frac{\pi}{n-2}\Gamma\left(\frac{n-3}{n-2}\right)\left(\frac{\gamma}{n-2}\right)^{1/(n-2)}, \quad (15)$$

$$A = B\tan\left(\Phi - \frac{\pi}{2(n-2)}\right), \quad (16)$$

$$C = \sqrt{\frac{n-2}{\pi}}\frac{B}{\cos\left(\Phi - \frac{\pi}{2(n-2)}\right)}. \quad (17)$$

The functions χ and χ_0 can now be used to calculate the effective range from the integral (8). The dominant contribution to the integral $\int \chi^2 dr$ comes from large distances $r > r^*$. Indeed, let us estimate this integral at $r \sim r^*$ using the semiclassical solution (13). Substituting $p = \sqrt{2\mu\alpha/r^n}$ and replacing $\sin^2()$ with $\frac{1}{2}$ we obtain

$$\int \chi^2 dr \approx \frac{C^2}{2}\int\frac{r^{n/2}dr}{\sqrt{2m\alpha}} = \frac{C^2 r^{n/2+1}}{\hbar\gamma(n+2)}. \quad (18)$$

This shows that the contribution of the semiclassical part of the wave function, and small distances on the whole, is negligible, and the expression for χ in terms of the Bessel functions, Eq. (14), can be used for all r.

Both $\int^r \chi_0^2 dr$ and $\int^r \chi^2 dr$ are divergent as r goes infinity; however, these divergences must cancel to produce a finite r_e. The first integral is trivial,

$$\int_0^r \chi_0^2 dr = r - \frac{r^2}{a} + \frac{r^3}{3a^2}, \quad (19)$$

and we should concentrate on the integration of the function χ^2. Using the well-known expression

$$N_\nu(x) = \frac{1}{\sin\nu\pi}[\cos\nu\pi J_\nu(x) - J_{-\nu}(x)], \quad (20)$$

and the expressions for A and B from Eqs. (15) and (16), as well as Eqs. (4) and (5), we have

$$\int \chi^2 dr = -\nu 2^{4\nu+1}(\gamma\nu)^{2\nu}\left\{[\Gamma(1+\nu)]^2\int x^{-(4\nu+1)}\right.$$
$$\times[J_\nu(x)]^2 dx - \frac{2(\gamma\nu)^{2\nu}}{a}\Gamma(1-\nu)$$
$$\times\Gamma(1+\nu)\int x^{-(4\nu+1)}J_\nu(x)J_{-\nu}(x)dx$$
$$\left. +\frac{(\gamma\nu)^{4\nu}}{a^2}[\Gamma(1-\nu)]^2\int x^{-(4\nu+1)}[J_{-\nu}(x)]^2 dx\right\}, \quad (21)$$

where $\nu = 1/(n-2)$ and $x = 2\gamma\nu r^{-1/2\nu}$ is the new integration variable. The divergence now comes from the lower limits where $J_{\pm\nu}\propto x^{\pm\nu}$. The next step is to integrate by parts and single out the divergence within the surface terms. For example, the first integral is transformed as

$$\int x^{-(4\nu+1)}[J_\nu(x)]^2 dx = -\frac{1}{2\nu}[x^{-2\nu}J_\nu(x)]^2$$
$$-\frac{1}{\nu}\int x^{-4\nu}J_\nu(x)J_{\nu+1}(x)dx, \quad (22)$$

where the remaining integral is well behaved at $x=0$, and has a finite value when calculated between 0 and ∞. After substitution into Eq. (21), the surface term and the integral part appear as

$$\int \chi^2 dr = 2^{4\nu}(\gamma\nu)^{2\nu}[\Gamma(1+\nu)]^2\left\{[x^{-2\nu}J_\nu(x)]^2\right.$$
$$\left. +2\int x^{-4\nu}J_\nu(x)J_{\nu+1}(x)dx\right\} +\cdots \quad (23)$$

for the first integral in Eq. (21). Since the expansion for the Bessel function for $x\ll 1$ $(r\to\infty)$ is

$$J_\nu(x) \simeq \frac{x^\nu}{2^\nu\Gamma(1+\nu)},$$

the surface term in Eq. (23) goes to infinity as $(2\gamma\nu)^{2\nu}x^{-2\nu}=r$ which cancels exactly the first divergent term of the integral (19), when we substitute both into Eq. (8). Similarly, the other two divergent terms on the right hand side are removed by the surface terms of the second and third integrals in Eq. (21), respectively. Finally, the remaining integrals are finite and have simple analytical answers [7].

As a result, the effective range is obtained in the form

$$r_e = F_n - \frac{G_n}{a} + \frac{H_n}{a^2}, \quad (24)$$

where F_n, G_n, and H_n depend only on the asymptotic parameters γ and $\nu = 1/(n-2)$:

$$F_n = \frac{2}{3}\frac{\pi}{\sin\nu\pi}(\gamma\nu)^{2\nu}\frac{\Gamma(\nu)\Gamma(4\nu)}{[\Gamma(2\nu)]^2\Gamma(3\nu)}, \quad (25)$$

$$G_n = \frac{4}{3}\frac{\pi}{\sin\nu\pi}(\gamma\nu)^{4\nu}\frac{\Gamma(1-2\nu)\Gamma(4\nu)}{\nu\Gamma(\nu)\Gamma(2\nu)\Gamma(3\nu)}, \quad (26)$$

$$H_n = \frac{2}{3}\frac{\pi}{\sin\nu\pi}(\gamma\nu)^{6\nu}\frac{\Gamma(1-3\nu)\Gamma(1-\nu)\Gamma(4\nu)}{\nu^2[\Gamma(\nu)]^2[\Gamma(2\nu)]^2}, \quad (27)$$

which, apart from some numerical factors, scale as $F_n \sim \bar{a}$, $G_n \sim \bar{a}^2$, and $H_n \sim \bar{a}^3$ [see Eq. (5)]. Therefore, the effective range in this problem is not an independent parameter, but a simple function of the mean scattering length $\bar{a}$ and the true scattering length a. The typical value of r_e is determined by

the long-range behavior of $U(r)$ in terms of γ, the way it determines the characteristic mean scattering length $\bar{a}$. The particular values of r_e and the scattering length a are decided by the short-range part of the potential curve, which determines the actual magnitude of the zero-energy semiclassical phase Φ.

This means that if one considers two different interatomic potentials characterized by the same asymptotic behavior (equal γ) and phases Φ that differ by an integer multiple of π, such potentials will produce the same scattering length and effective range. As a result the s-phase shifts in these potentials will be essentially the same at low scattering momenta $k\bar{a}\ll 1$, Eq. (1). As we show in Sec. IV this statement is in fact valid in a much larger range of momenta, $k\bar{a}>1$, provided the scattering energy is much smaller than the characteristic minimum depth of the potential curve.

The asymptotic part of the atomic interaction, i.e., the van der Waals constant C_6, is usually known much better than the details of the potential curve at smaller distances. The present calculation shows that the low-energy scattering is sensitive to these details to the extent that they influence the semiclassical phase. From this point of view Φ and γ are the best parameters to describe the low-energy atomic scattering. In conclusion we present the results of our calculation in the physically important case $n=6$ ($\nu=\frac{1}{4}$) for the scattering length

$$a=\bar{a}[1-\tan(\Phi-\pi/8)], \qquad (28)$$

$$\bar{a}=\sqrt{2\gamma}\,\Gamma(\tfrac{3}{4})/\Gamma(\tfrac{1}{4})\approx 0.477\,989\sqrt{\gamma}, \qquad (29)$$

and the effective range

$$r_e=\frac{\sqrt{2\gamma}}{3}\left[\frac{\Gamma\!\left(\frac{1}{4}\right)}{\Gamma\!\left(\frac{3}{4}\right)}-2\frac{\sqrt{2\gamma}}{a}+\frac{\Gamma\!\left(\frac{3}{4}\right)}{\Gamma\!\left(\frac{1}{4}\right)}\frac{4\gamma}{a^2}\right] \qquad (30)$$

$$=\frac{\bar{a}}{3}\left[\frac{\Gamma\!\left(\frac{1}{4}\right)}{\Gamma\!\left(\frac{3}{4}\right)}\right]^2\left[1-2\frac{\bar{a}}{a}+2\left(\frac{\bar{a}}{a}\right)^2\right] \qquad (31)$$

$$\approx\sqrt{\gamma}\left(1.394\,73-1.333\,33\frac{\sqrt{\gamma}}{a}+0.637\,32\frac{\gamma}{a^2}\right). \qquad (32)$$

Expression (31) makes it clear that in agreement with the general theory r_e is always positive.

III. NUMERICAL EXAMPLES

To test our analytical formula for r_e we first refer to Refs. [3–5], where the scattering lengths and effective ranges were obtained for alkali atoms by direct numerical solution of the Schrödinger equation. Their results for Li, Na, and Cs pairs interacting via singlet and triplet potentials are shown in Table I. Using the asymptotic parameters γ and the scattering lengths a from the above calculations we calculate the effective ranges analytically from Eq. (32), sixth column of

TABLE I. The scattering length a and effective range r_e (in atomic units) for alkali-metal atom scattering.

Atoms	State	γ^a (a.u.)	a	r_e	$r_e{}^b$
Li-Li	$^1\Sigma_g$	4213.3	36.9[c]	66.5[c]	66.3
	$^3\Sigma_u$		-17.2[c]	1014.8[c]	1006.3
Na-Na	$^1\Sigma_g$	7854.2	34.936[d]	187.5[d]	187.3
	$^3\Sigma_u$		77.286[d]	62.5[d]	62.4
Cs-Cs	$^3\Sigma_u$	41234.0	68.216[e]	624.55[e]	624.01

[a]$\gamma=\sqrt{2\mu C_6}$ obtained using the reduced masses $\mu=6394.7$, 20954, and 1.211×10^5 a.u., and $C_6=1388$, 1472, and 7020 a.u. for $^7\text{Li}_2$, $^{23}\text{Na}_2$, and $^{133}\text{Cs}_2$, respectively.
[b]Calculated analytically from Eq. (32).
[c]Calculated numerically in [5].
[d]Calculated numerically in [3,5].
[e]Obtained numerically in [4], using the potential from [2] with the cutoff radius $r_c=23.165$ a.u.

Table I. Our values of r_e agree to better than 1% with the numerical ones (fifth column), which clearly demonstrates the accuracy of our semiclassical approach in low-energy atomic collisions. This also confirms that in atomic scattering r_e is not really an independent parameter of the s-phase-shift expansion (1).

As a further illustration, let us consider the phase shifts produced by two different potentials with the same asymptotic behavior. The first one is the $\text{Cs}_2\,{}^3\Sigma_3$ interpolation potential of Ref. [2],

$$U(r)=\frac{1}{2}Br^\lambda e^{-\eta r}-\left(\frac{C_6}{r^6}+\frac{C_8}{r^8}+\frac{C_{10}}{r^{10}}\right)f_c(r), \qquad (33)$$

where the first item on the right-hand side represents the exchange repulsion between the valence electrons, and $f_c(r)$ in the long-range part is a cutoff function that cancels the $1/r^n$ divergence at small distances:

$$f_c(r)=\theta(r-r_c)+\theta(r_c-r)e^{-(r_c/r-1)^2}, \qquad (34)$$

where $\theta(x)$ is the unit step function, $\theta(x)=1(0)$, when $x>(<)0$. The values of the parameters $B=0.0016$, $\lambda=5.53$, $\eta=1.072$, $C_6=7020$, $C_8=1.1\times 10^6$, and $C_{10}=1.7\times 10^8$ a.u. of the potential (33) are from [8]. The cutoff radius $r_c\approx 23$ a.u. can be viewed as a free parameter, due to a lack of accurate *ab initio* calculations or experimental information about the potential [9].

The second potential is the simple Lennard-Jones potential

$$U(r)=\frac{\beta}{r^m}-\frac{\alpha}{r^n}\quad (m>n). \qquad (35)$$

For this potential the semiclassical phase (6) is given by

$$\Phi=\sqrt{2\mu}\,\alpha^{(m-2)/2(m-n)}\beta^{-(n-2)/2(m-n)}$$
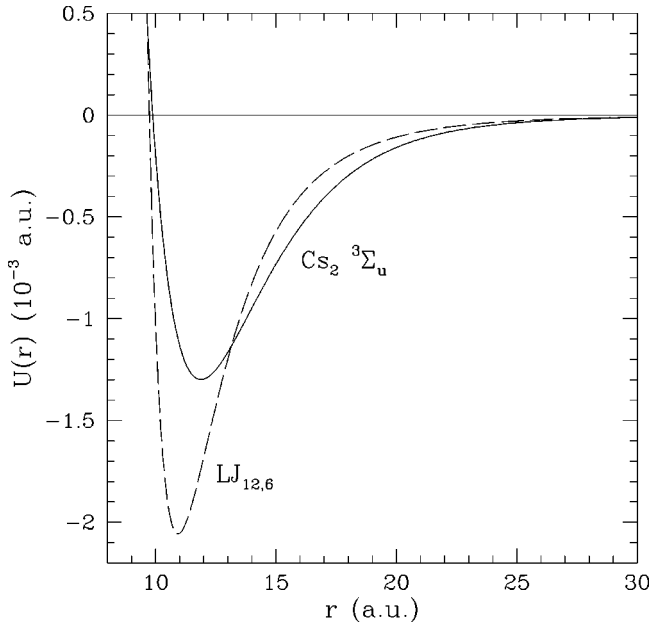$$\times\frac{1}{m-n}B\left(\frac{3}{2},\frac{n-2}{2(m-n)}\right), \qquad (36)$$

FIG. 1. $Cs_2 {}^3\Sigma_u$ potential of Eq. (33) with $r_c = 23.165$ a.u. and the Lennard-Jones 12-6 potential with the same asymptotic behavior and semiclassical phase $\Phi = 182.895$.

where $B(\ )$ is the beta function, and the scattering length and effective range are calculated analytically from Eqs. (4) and (24). Interatomic potentials are often approximated by Eq. (35) with $m = 12$ and $n = 6$ (the so-called Lennard-Jones 12-6 potential, $LJ_{12,6}$), and we will stick to this case hereafter. Then

$$\Phi = \sqrt{2\mu}\,\alpha^{5/6}\beta^{-1/3}\frac{\sqrt{\pi}\Gamma(\tfrac{1}{3})}{10\Gamma(\tfrac{5}{6})} \approx 0.420\,654\,63\sqrt{2\mu}\,\alpha^{5/6}\beta^{-1/3}.$$

$$(37)$$

Our theory asserts that the two potentials (33) and (35) (with $\alpha = C_6$) should give the same values of a, r_e, and in fact the same low-energy s-phase shifts, provided they have equal semiclassical phases Φ, even though the potential curves at small r can be quite different; see Fig. 1.

To test this we calculate the s-wave phase shifts for Cs atoms ($\mu = 1.211 \times 10^5$ a.u.) using the $Cs_2 {}^3\Sigma_3$ potential with five different cutoff radii; see Table II. We do it by solving the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{dr^2} + U(r)\chi(r) = E\chi(r) \qquad (38)$$

numerically at $E = \hbar^2 k^2/2\mu$, and finding δ_0 from the asymptotic behavior of the wave function $\chi(r) \sim \sin(kr + \delta_0)$ [10]. The phases at small k are used to extract the scattering length numerically from Eq. (1). We also calculate the zero-energy semiclassical phases Φ for these potentials, and obtain the values of a and r_e from Eqs. (28), (29), and (32), using $\gamma = 41\,234.0$ a.u.

Once Φ is known, we consider scattering in the

TABLE II. Comparison of the scattering lengths obtained numerically for the $Cs_2 {}^3\Sigma_u$ and $LJ_{12,6}$ potentials and, analytically, using the semiclassical theory.

		Scattering lengths (a.u.)			
r_c[a]	Φ	$Cs_2 {}^3\Sigma_u$[b]	$LJ_{12,6}$[b]	Eq. (28)[c]	r_e[c]
23.115	184.4258016	477.16	477.86	477.29	191.45
23.140	183.6562031	−72.23	−72.44	−72.59	2053.28
23.165	182.8954135	68.24	68.13	68.06	627.41
23.190	182.1432966	145.45	145.43	145.37	157.54
23.215	181.3997181	350.65	351.02	350.73	169.84

[a]Smaller cutoff radii correspond to stronger (deeper) potentials and, consequently, greater semiclassical phases Φ.
[b]Scattering lengths obtained from numerical δ_0 using Eq. (1) at $k \to 0$.
[c]Analytical calculation by means of Eqs. (28), (29), and (32) using Φ from the second column and $\gamma = 41\,234.0$.

$LJ_{12,6}$ potential (35), with $\alpha = C_6 = 7020$ a.u. and $\beta = (0.420\,654\,63\sqrt{2\mu}C_6^{5/6}/\Phi)^3$, which ensures that this potential returns the same semiclassical phase (37). The low-energy scattering phase shifts produced by the two potentials are shown in Fig. 2, and the scattering lengths are compared in Table II. The difference between the scattering lengths in the $Cs_2 {}^3\Sigma_3$ and $LJ_{12,6}$ potentials in Table II does not exceed 0.3%. The scattering lengths obtained analytically from Eq. (28) are also very close to the numerical ones. Moreover, the s-phase shifts from the two potentials are almost indistinguishable in Fig. 2, and the low-energy phase-shift fits (1) in terms of a and r_e are in good agreement with the numerical values. For the potential with the Cs_2 asymptotic behavior the mean scattering length from Eq. (29) is large, $\bar{a}$
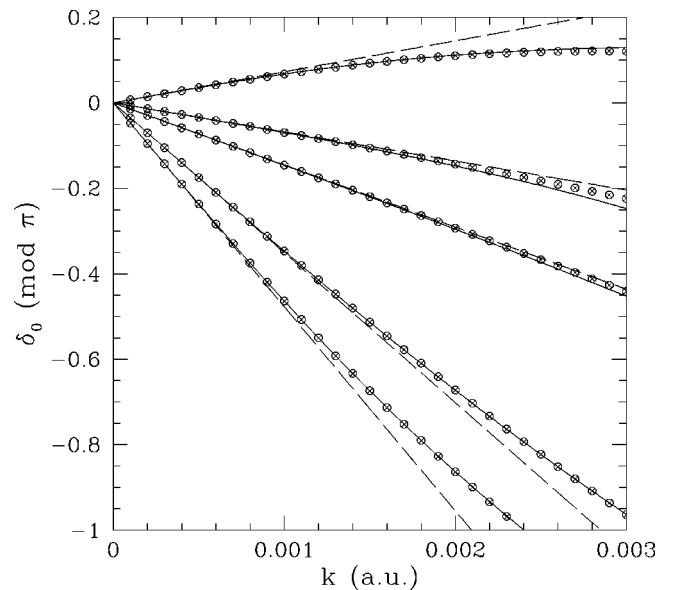

FIG. 2. s-wave phase shifts calculated in the $Cs_2 {}^3\Sigma_3$ potential of Eq. (33) with different cutoff radii (circles) and in the $LJ_{12,6}$ potentials with equal phases Φ (crosses). Dashed line is $\delta_0 = -ak$ and solid line is δ_0 from Eq. (1), with a and r_e obtained from Eqs. (28), (29), and (32); see Table II.
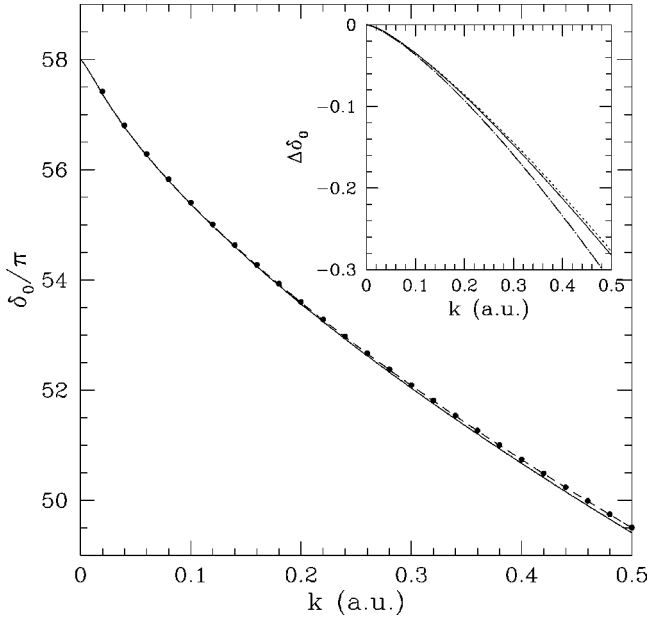
FIG. 3. s-wave phase shifts calculated in the Cs_2 $^3\Sigma_u$ potential of Eq. (33) with $r_c = 23.165$ a.u. (solid line) and in the $LJ_{12,6}$ potentials with the same asymptotic behavior and phase Φ (dashed line). Solid circles show the semiclassical result (46). Shown in the inset is the difference between δ_0 in the Cs_2 $^3\Sigma_u$ and $LJ_{12,6}$ potentials, and the corresponding correction due to the $-C_8/r^8$ term, obtained as a difference between Eqs. (47) and (46) (dotted line) and, in the first order in C_8, from Eq. (49) (dot-dashed line).

$= 97.1$ a.u., and the validity of Eq. (1) is limited to $k \ll \bar{a}^{-1} \approx 0.01$ a.u.

IV. SEMICLASSICAL CALCULATION OF THE PHASE SHIFT

We saw in Fig. 2 that the phase shifts produced by the two different potentials from Fig. 1 are practically the same at small k. Let us now look at 100 times greater momenta that go well beyond the validity range of expansion (1). Figure 3 shows that the two potentials still give very close phase shifts. If we change the cutoff radius of the Cs_2 $^3\Sigma_u$, thereby changing the strength of the potential well, the phase shifts on a large momentum scale go ''parallel'' (Fig. 4). At small k they of course behave differently, as prescribed by their scattering lengths (Table II, Fig. 4 inset). In accordance with Levinson's theorem at $k \to 0$ the phase shifts go to $N_s \pi$, where N_s is the number of s bound states in the potential (58 or 59, depending on r_c).

At small distances, Eq. (38) at $E > 0$ can be treated using the semiclassical approximation, as the increase of p only improves its applicability; see Eqs. (11) and (12). At large distances, $U(r) \to 0$, and $p \to \hbar k$; thus, the semiclassical approximation is also valid at $r \to \infty$. Therefore, it may only be violated somewhere in between. Indeed, when we analyze the left-hand side of Eq. (11) using the asymptotic form (3), we see that it has a maximum at $r^n = (n-2)\alpha/[2(n+1)E]$. If we require that the height of this maximum be $\ll 1$, we obtain

$$k \gg \gamma^{-2/(n-2)} \quad \text{or} \quad k\bar{a} \gg 1, \qquad (39)$$
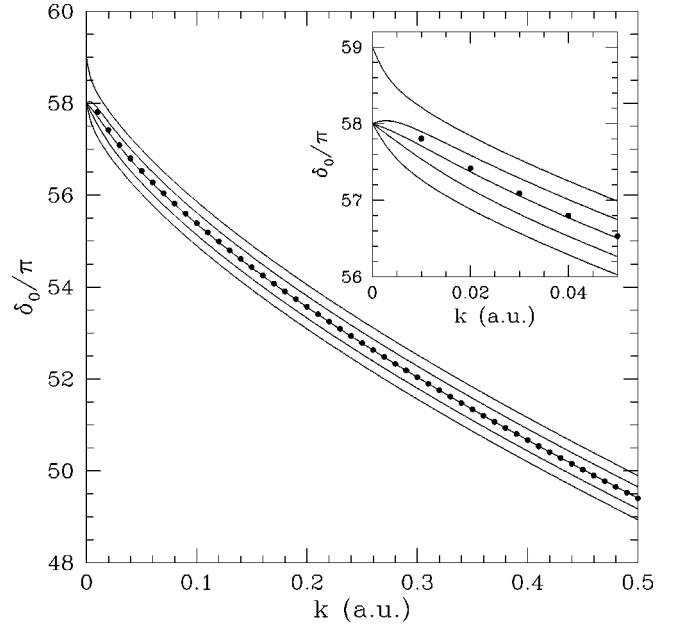

FIG. 4. Solid lines show the s-wave phase shifts calculated in the Cs_2 $^3\Sigma_u$ potential of Eq. (33) with different cutoff radii; see Table II. Solid circles show the semiclassical analytical result Eq. (46) with the correction, Eq. (49), phase, calculated using $\gamma = 41\,234.0$ a.u., $\Phi = 182.8954$, and $C_8 = 1.1 \times 10^8$ a.u.

where we dropped the n-dependent numerical factor ~ 1 on the right-hand side of the first inequality, and used Eq. (5) in the second. Note that this condition is just opposite to $k\bar{a} \ll 1$, where expansion (1) is valid, and where we have been able to solve the scattering problem analytically by calculating a and r_e.

Now we will calculate the phase shift for $k\bar{a} \gg 1$ purely semiclassically. Wave function (13) with $p = \sqrt{2\mu[E - U(r)]}$ is now valid everywhere and the phase shift is

$$\delta_0(k) = \lim_{r \to \infty} \left(\frac{1}{\hbar} \int_{r_0}^{r} p\,dr - kr \right) + \frac{\pi}{4}. \qquad (40)$$

For $k \to 0$ the integral on the right-hand side (RHS) approaches Φ of Eq. (6). The difference between large $\delta_0(k)$ and Φ remains relatively small in a wide range of k (see Fig. 3), as long as $E \ll |U_{\min}|$, where $U_{\min}$ is the characteristic depth of the potential curve minimum at $r = r_{\min}$. Thus, we proceed with the calculation of δ_0 as follows (using atomic units with $\hbar = 1$ below):

$$\delta_0(k) = \int_{r_0}^{\infty} [\sqrt{k^2 - 2\mu U(r)} - k$$

$$- \sqrt{-2\mu U(r)}]\,dr - kr_0 + \Phi + \frac{\pi}{4}. \qquad (41)$$

The integral above converges at $r \to \infty$ as $U(r) \to 0$. At smaller distances where $2\mu|U(r)| \gg k^2$ the two square roots essentially cancel each other,

$$\sqrt{k^2 - 2\mu U(r)} - \sqrt{-2\mu U(r)} \simeq \frac{k^2}{2\sqrt{2\mu|U(r)|}}, \quad (42)$$

and the corresponding contribution to the integral is estimated as $k r_{\min}\sqrt{E/|U_{\min}|}$; hence it is small. The important distances in the integral in Eq. (41) are those where $k^2 \sim 2\mu|U(r)|$; therefore, for $E \ll |U_{\min}|$ we can replace $U(r)$ by its asymptotic form and integrate formally from zero to infinity:

$$\int_0^\infty \left(\sqrt{k^2 + \frac{\gamma^2}{r^n}} - k - \sqrt{\frac{\gamma^2}{r^n}} \right) dr$$

$$= -[\gamma^{2/(n-2)} k]^{(n-2)/n} \int_0^\infty (1 + t^{-n/2} - \sqrt{1 + t^{-n}}) dt. \quad (43)$$

The dimensionless integral I_n on the RHS calculated by parts as

$$I_n = \frac{n}{2} \int_0^\infty \frac{x^{n/2} dx}{\sqrt{1 + x^n}(1 + \sqrt{1 + x^n})} = \frac{n \Gamma\left(1 - \frac{1}{n}\right) \Gamma\left(\frac{1}{2} + \frac{1}{n}\right)}{(n-2)\sqrt{\pi}}. \quad (44)$$

Thus, starting from Eq. (41) we have obtained the following expression for the phase shift [11]:

$$\delta_0(k) = \Phi + \frac{\pi}{4} - I_n[\gamma^{2/(n-2)} k]^{(n-2)/n}. \quad (45)$$

For the physically important case $n = 6$,

$$\delta_0 = \Phi + \frac{\pi}{4} - I_6 \gamma^{1/3} k^{2/3}, \quad (46)$$

where $I_6 = \frac{3}{2}\Gamma(\frac{5}{6})\Gamma(\frac{2}{3})/\sqrt{\pi} \approx 1.293\,55$.

Figure 3 illustrates that Eq. (46) works well for $k > \bar{a}^{-1} \approx 0.01$ a.u. It means that the two parameters Φ and γ indeed determine the energy dependence of the phase shifts in the wide range of momenta. One cannot help noticing, though, that the semiclassical formula clearly favors the phase shift in the $LJ_{12,6}$ potential. The difference between δ_0 in the two potentials shown in the inset of Fig. 3 suggests that it increases as $\sim k^\lambda$ with $1 < \lambda < 2$. If this difference were due to the difference between the two potential curves at small distances (Fig. 1), it would be proportional to k^2, as follows from Eq. (42). Thus, we have to conclude that it is due to the different asymptotic behavior of the potentials (33) and (35), namely, due to the next long-range term $-C_8/r^8$ in the Cs_2 $^3\Sigma_u$ potential. To take this effect into account one can simply calculate the semiclassical phase shift as

$$\int_0^\infty \left(\sqrt{k^2 + \frac{\gamma^2}{r^n} + \frac{2\mu C_m}{r^m}} - k \right.$$

$$\left. - \sqrt{\frac{\gamma^2}{r^n} + \frac{2\mu C_m}{r^m}} \right) dr + \Phi + \frac{\pi}{4}; \quad (47)$$

cf. Eqs. (41) and (43), $m > n$. Unlike Eq. (43) this expression cannot be evaluated analytically, but its numerical calculation is straightforward (e.g., using MATHEMATICA [12]). The difference between the phase shifts (47) and (46) obtained with $m = 8$, $\gamma = 41\,234.0$, and $C_8 = 1.1 \times 10^8$ a.u. is shown in Fig. 3 (inset) by the dotted line. It is in very good agreement with the difference between phase shifts found numerically from the Schrödinger equation for the two potentials.

If we consider the second long-range term in Eq. (47) as a correction, the integral can be expanded in powers of C_m. The total phase shift is then presented as $\delta_0(k) + \Delta\delta_0(k)$, where $\delta_0(k)$ is given by Eq. (45), and the correction is given by

$$\Delta\delta_0(k) = -\mu C_m \gamma^{-2(m-1)/n} k^{2(m-1)/n - 1}$$

$$\times \frac{\Gamma\left(\frac{3}{2} - \frac{m-1}{n}\right)\Gamma\left(\frac{m-1}{n}\right)}{\left(m - 1 - \frac{n}{2}\right)\sqrt{\pi}} \quad (48)$$

$$\approx -0.350\,545 \mu C_8 \gamma^{-7/3} k^{4/3} \quad (n = 6,\ m = 8). \quad (49)$$

In spite of a relatively large numerical value of C_8 for Cs the last expression is also in good agreement with the numerical $\Delta\delta_0$ (Fig. 3, inset). Figure 4 demonstrates that the sum of the semiclassical phase (46) and correction (49) provides an accurate description of the momentum dependence of the s-wave phase shift for the Cs atoms.

V. CONCLUSIONS

We have shown that the s-wave scattering properties of atoms in a wide range of momenta depend only on the zero-energy semiclassical phase Φ of the potential and its long-range asymptotic behavior dominated by the $-C_6/r^6$ term. The latter influences the result through the large parameter $\gamma = \sqrt{2\mu C_6}$, which explains the large values of atom-atom cross sections at low energies (through the mean scattering length $\bar{a}$) and governs the energy dependence of the phase shifts. At small momenta $k < \bar{a}^{-1}$ the phase shift is determined by the scattering length a and effective range r_e. We have obtained a formula which shows that r_e is a function of γ and a. At larger momenta $k > \bar{a}^{-1}$ the phase shift has been calculated semiclassically, and possible corrections due to other long-range terms in the potential have been estimated. In particular this means that atomic scattering, as well as the positions of diatomic vibrational bound states near the dissociation limit [13], is relatively insensitive to the shape of the potential curve at small distances, provided the zero-energy semiclassical phase is fixed.

Note added in proof. Recently we found that Eq. (30) for the effective range has been obtained by Gao [14] from the exact theory of wave functions in the long-range potential with $n = 6$.

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[10] To facilitate this we in fact compare the phase of the numerical $\chi(r)$ with the expression that includes corrections due to the long-range terms in the potential analytically: $\chi(r) \sim \sin\{kr + \delta_0 - (1/2k)[(C_6/5)r^{-5} + (C_8/7)r^{-7} + (C_{10}/9)r^{-9}]\}$.

[11] A similar calculation of the semiclassical phase at *negative* energies $E = -\kappa^2\hbar^2/2\mu$ yields $\Phi(E) = \Phi - \sqrt{\pi}\gamma^{2/n}\kappa^{(n-2)/n}\Gamma(\frac{1}{2}+1/n)/[(n-2)\Gamma(1+1/n)]$. It is often used for studying quantization of vibrational levels near the dissociation limit in diatomic molecules, R. J. LeRoy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970); J. Trost, C. Eltschka, and H. Friedrich, J. Phys. B **31**, 361 (1998).

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