Computation of the scattering length and effective range in molecular physics

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A simple and easily implemented highly accurate method to compute the scattering length and effective range for a diatomic potential is presented. It combines the numerical solution for small internuclear distances R with analytical corrections for large R. The method provides upper and lower limits to the exact values, to any desired precision. A numerical example and discussion are given for the case of the Cs-Cs ground-state interaction.

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I. INTRODUCTION

Knowledge of the scattering length and effective range for diatomic potentials is of fundamental importance in the study of low-energy, low-temperature collisions. We present here a fast and very accurate method to compute the scattering length and effective range for diatomic potential curves.

A typical potential curve is constructed for small values of the internuclear distance R from *ab initio* data, usually computed variationally, and for large R by a polynomial in inverse powers of R with specified coefficients. We will not present the details of constructing such potential curves, but we do require that beyond a certain value of R the potential curves can be represented by a known simple analytical form.

For a spherical symmetric potential $V(R)$ which vanishes at infinity equal or faster than $1/R^4$, the scattering length is defined from the asymptotic behavior of the solution $U(R)$ of the radial Schrödinger equations at energy equal to zero:

$$\frac{d^2U}{dR^2}=2MV(R)U(R)\ ,$$
$$U(0)=0\ , \tag{1}$$
$$U(R)=\alpha R+\beta \ \text{ as } R\to\infty\ ,$$

where M is the reduced mass of the system and α and β are constants. The scattering length is given by

$$a=-\frac{\beta}{\alpha}\ , \tag{2}$$

and the effective range by [1]

$$r_0=\frac{2}{\beta^2}\int_0^\infty [U_0^2(R)-U^2(R)]dR\ , \tag{3}$$

where U_0 is the asymptote of U,

$$U_0(R)=\alpha R+\beta\ . \tag{4}$$

For the case of an attractive potential decreasing at infinity like $1/R^4$, U_0 should be replaced by [2]

$$U_0(R)=\alpha R\cos\frac{\sqrt{C_4}}{R}+\beta\frac{R}{\sqrt{C_4}}\sin\frac{\sqrt{C_4}}{R}\ , \tag{5}$$

where C_4 is $2M$ times the coefficient of $1/R^4$ in the analytical expression of the potential for large R.

The direct numerical integration of Eq. (1) give rise to many numerical problems because the asymptotic behavior of the solution is reached only at very large distances, usually tens of thousands of atomic units. In Sec. II we will present a method to integrate Eq. (1) safely. The method consists of combining the numerical solution for small R, where the potential usually is known numerically, with the analytical solution for large R, where the potential has a simple analytical form. For the case of an attractive potential, the method itself controls the errors, providing upper and lower limits to the convergence. An example of the method will be given in Sec. III for the case of the Cs-Cs ground-state interaction, using the model potential curve from [3]. For this case there are previous evaluations of the scattering length which will serve as comparisons.

II. THEORY

Let $\mathcal{V}(R)$ be the potential $V(R)$ multiplied by $2M$ and introduce the following *ansatz* for the solution of Eq. (1) at large R:

$$U(R)=\alpha\varepsilon_\alpha(R)+\beta\varepsilon_\beta(R)\ , \tag{6}$$

where the functions $\varepsilon_\alpha(R)$ and $\varepsilon_\beta(R)$ tend to R and unity, respectively, as R goes to infinity. Introducing Eq. (6) into Eq. (1) we get the following differential equations for ε_α and ε_β,

$$\varepsilon_\gamma''=\mathcal{V}\varepsilon_\gamma,\ \ \varepsilon_\gamma\to\varphi_\gamma \text{ as } R\to\infty\ , \tag{7}$$

where γ could be either α or β and $\varphi_\alpha=R$ and $\varphi_\beta=1$. In the general case, the potential $\mathcal{V}(R)$ at large R is given by a polynomial in inverse powers of R. Equation (7) cannot be solved exactly, but the solution can be given by a series of successive approximations which are the solutions of the following system of equations:

$$\varepsilon_\gamma^{(k+1)''}=\mathcal{V}\varepsilon_\gamma^{(k)},\ \ \varepsilon_\gamma^{(0)}=\varphi_\gamma\ , \tag{8}$$

where $\lim_{k\to\infty}\varepsilon_\gamma^{(k)}=\varepsilon_\gamma$.

Let δ_γ denote the difference between two consecutive approximations of ε_γ, so that

$$\delta_\gamma^{(k)}=\varepsilon_\gamma^{(k)}-\varepsilon_\gamma^{(k-1)},\quad \delta_\gamma^{(0)}=\varphi_\gamma\ . \tag{9}$$

With these notations Eq. (6) becomes

$$U(R)=\alpha(R+\delta_\alpha^{(1)}+\delta_\alpha^{(2)}+\cdots)+\beta(1+\delta_\beta^{(1)}+\delta_\beta^{(2)}+\cdots)\ , \tag{10}$$

where $\delta_\alpha^{(k)}$ and $\delta_\beta^{(k)}$ are functions of R which vanish at infinity and which are the solutions of the following system of equations:

$$\delta_\gamma^{(k+1)''}=\mathcal{V}\delta_\gamma^{(k)} \text{ for } k=0,1,\ldots\ . \tag{11}$$

The system of equations (11) can be easily integrated since the potential $\mathcal{V}$ is a polynomial in inverse powers of R, and so are the solutions. For large R the convergence of Eq. (10) with the computed δ corrections is very fast. If n is the smallest power of $1/R$ in the potential $\mathcal{V}$, then the smallest power of $1/R$ in the kth order corrections will be $n(k-2)-1$ for $\delta_\alpha^{(k)}$ and $n(k-2)$ for $\delta_\beta^{(k)}$. In practice it will be enough to compute the first three or four corrections in order to insure a good approximation for the solution of Eq. (1), for R of the order of a few hundred atomic units.

Once Eq. (9) is established the constants α and β are determined by matching with the numerical solution computed for $R<R_0$. The numerical integration can be carried out in the usual fashion [4] since the range of integration is not larger than a few hundred atomic units, a common range in atomic physics.

Let u and u' be the numerical values of the solution of Eq. (1) and its derivative at the matching point R_0. Then the scattering length is given from Eq. (2) by

$$a=\frac{u\varepsilon_\alpha^{(k)'}-u'\varepsilon_\alpha^{(k)}}{u\varepsilon_\beta^{(k)'}-u'\varepsilon_\beta^{(k)}}\ , \tag{12}$$

and the effective range from Eq. (3) by

$$r_0=\tfrac{2}{3}R_0\left[\left(\frac{R_0}{a}\right)^2-3\frac{R_0}{a}+3\right]-\frac{2}{\beta^2}\int_0^{R_0}U^2(R)dR-2\int_{R_0}^{\infty}S_k\left[2-\frac{2}{a}R+S_k\right]dR\ , \tag{13}$$

where

$$S_k=\sum_{l=1}^{k}\left[\delta_\beta^{(l)}-\frac{1}{a}\delta_\alpha^{(l)}\right]\ , \tag{14}$$

and k is the highest order of δ corrections included in the computation. For the case of the attractive potential decreasing at infinity as $1/R^4$ the effective range has the following expression:

$$r_0=\chi(R_0)-\frac{2}{\beta^2}\int_0^{R_0}U^2(R)dR+2\int_{R_0}^{\infty}\left[\left(\frac{R}{\sqrt{C_4}}\sin\frac{\sqrt{C_4}}{R}-\frac{R}{a}\cos\frac{\sqrt{C_4}}{R}\right)^2-\left(1-\frac{R}{a}+S_k\right)^2\right]dR\ , \tag{15}$$

where

$$\chi(R_0)=\frac{1}{a\sqrt{C_4}}\left[-\frac{2}{a}R_0^3+\left(1-\frac{C_4}{a^2}\right)R_0^2+\frac{4C_4}{a}R_0\right]\sin\left[\frac{2C_4}{R_0}\right]+\tfrac{1}{3}\left[-C_4\left(1-\frac{C_4}{a^2}\right)R_0^3-\frac{2}{a}R_0^2+2\left(1-\frac{C_4}{a^2}\right)R_0\right]\cos\left[\frac{2C_4}{R_0}\right]+\tfrac{4}{3}\sqrt{C_4}\left(1-\frac{C_4}{a^2}\right)\mathrm{Si}\left[\frac{2C_4}{R_0}\right]-\frac{8C_4}{3a}\mathrm{Ci}\left[\frac{2C_4}{R_0}\right]+\frac{1}{3C_4}\left[1+\frac{C_4}{a^2}\right]R_0^3-\frac{2\pi}{3}\sqrt{C_4}\left[1-\frac{C_4}{a^2}\right]\ . \tag{16}$$

The second integral from Eq. (15) is convergent and can be solved analytically in terms of sin, cos, Si, and Ci functions. If C_4/R_0 is a small quantity, an expansion in inverse powers of R may be more appropriate. We recommend the use of MAPLE or another symbolic mathematical language in order to solve Eq. (11) as well as the second integral from Eq. (13) or (15).

It is clear that the value of scattering length a, and the value of the effective range r_0 depend on the number of corrections included in the computation. If $a^{(k)}$ and $r_0^{(k)}$ are the values of scattering length and effective range computed, at a given value of R_0, using up to the kth δ corrections, then the sets $\{a^{(k)}\}_{k\in\mathbf{N}}$ and $\{r_0^{(k)}\}_{k\in\mathbf{N}}$ converge to the exact value a and r_0 respectively.

For the case of an attractive potential and for a large value of the matching point R_0 we will show that the sets $\{a^{(k)}\}_{k\in\mathbf{N}}$ and $\{r_0^{(k)}\}_{k\in\mathbf{N}}$ approach their limits by successive upper and lower limiting values. To do so it is enough to show that the sets $\{a^{(k+1)}-a^{(k)}\}_{k\in\mathbf{N}}$ and $\{r_0^{(k+1)}-r_0^{(k)}\}_{k\in\mathbf{N}}$ are alternate convergent sets.

First we observe from Eq. (11) that for a large value of R and for an attractive potential $\mathcal{V}$ given by a polynomial in inverse powers of R,

$$\mathrm{sgn}(\delta_\alpha^{(k)})=\mathrm{sgn}(\delta_\beta^{(k)})=(-1)^k\ . \tag{17}$$

Equation (12) can be rewritten as

$$a^{(k)}=\frac{\left[\frac{\varepsilon_\alpha^{(k)}}{U}\right]'_{R_0}}{\left[\frac{\varepsilon_\beta^{(k)}}{U}\right]'_{R_0}}, \tag{18}$$

where the quantities on the right-hand side are computed at R_0. Using Eq. (18) it can be shown that neglecting quadratic and higher terms in $\delta_\gamma^{(k)}$ and $\delta_\gamma^{(k)'}$ for $k\geq 1$ we have,

$$a^{(k+1)}-a^{(k)}\simeq T^{(k+1)}(R_0)-T^{(k+1)'}(R_0)\frac{u}{u'} -\delta_\beta^{(k+1)'}(R_0)\left[\frac{u}{u'}\right]^2, \tag{19}$$

where

$$T^{(k)}=\delta_\alpha^{(k)}-R\,\delta_\beta^{(k)}. \tag{20}$$

In the range of interest to our problem the solution of Eq. (1) is close to the asymptote and so U is an increasing function if U is positive and a decreasing function if it is negative. Hence the quantity u/u' in Eq. (19), computed at the matching point R_0, is positive. On the other hand, using Eq. (11) we get

$$T^{(k+1)''}=\mathcal{V}T^{(k)}-2\delta_\beta^{(k+1)'} \text{ with } T^{(0)}=0. \tag{21}$$

It is easy to see that for an attractive potential at large value of R, where the potential is given by a polynomial in inverse powers of R we have

$$\begin{aligned}\mathrm{sgn}(T^{(k+1)})&=-\mathrm{sgn}(T^{(k+1)'})\\&=-\mathrm{sgn}(\delta_\beta^{(k+1)'})\\&=\mathrm{sgn}(\delta_\beta^{(k+1)})=(-1)^{k+1}.\end{aligned} \tag{22}$$

Hence

$$\mathrm{sgn}(a^{(k+1)}-a^{(k)})=(-1)^{k+1}, \tag{23}$$

which ensures that the $\{a^{(k)}\}_{k\in\mathbf{N}}$ set approaches its limit though upper and lower values.

A similar conclusion holds for the effective range. Neglecting quadratic terms in $\delta_\gamma^{(k)}$ for $k\geq 1$ we have

$$r_0^{(k+1)}-r_0^{(k)}\simeq -4\int_{R_0}^{\infty}\left[\frac{R}{a^2}\delta_\alpha^{(k+1)}-\frac{1}{a}\delta_\alpha^{(k+1)} -\frac{R}{a}\delta_\beta^{(k+1)}+\delta_\beta^{(k+1)}\right]dR. \tag{24}$$

The integrand in Eq. (24) is a polynomial in inverse powers of R and so the integral will be a polynomial in inverse powers of R_0. For a large value of R_0 the sign of $r_0^{(k+1)}-r_0^{(k)}$ will be determined by the sign of the leading power of this polynomial, so that

$$\mathrm{sgn}(r_0^{(k+1)}-r_0^{(k)})=-\mathrm{sgn}(\delta_\alpha^{(k+1)})=(-1)^k. \tag{25}$$

Hence the set $\{r_0^{(k)}\}_{k\in\mathbf{N}}$ approaches its limit through upper and lower values.

In conclusion, for a given matching point R_0, the values of the scattering lengths and effective ranges, computed in consecutive orders of corrections, give the upper and lower bounds to the exact value. Let k be the largest order of δ corrections included in computation. Then, if k is an even number, the different values of scattering length, computed at different matching points R_0, will approach the exact value through upper values as R_0 goes to infinity and if k is an odd number by lower values. For the effective range the conclusion is reversed; for even k by lower values and for odd k by upper values. An illustration of these features will be presented in the next section.

III. NUMERICAL ILLUSTRATION

We used for our numerical example the model potential curve for the Cs-Cs ground-state interaction from [3] given by the following equation,

$$V(R)=\tfrac{1}{2}BR^{\mu}e^{-\eta R}-\left[\frac{C_6}{R^6}+\frac{C_8}{R^8}+\frac{C_{10}}{R^{10}}\right]f_c(R), \tag{26}$$

where the values of the constants are: $B=0.0016$, $\mu=5.53$, $\eta=1.072$, $C_6=7020$, $C_8=1.1\times 10^6$, and $C_{10}=1.7\times 10^8$. The cutoff function f_c has the following expression:

$$f_c(R)=\theta(R-R_c)+\theta(R_c-R)e^{-(R_c/R-1)^2}, \tag{27}$$

where θ is the step function and the values of the cutoff radius R_c are listed in the first column of Table I. The value of the cesium mass was taken, as in [3], to be $m_{\mathrm{Cs}}=2.422\times 10^5$ (a.u.).

This model contains all the features necessary for a good candidate to test our method for computing the scattering length and effective range. The shape of the potential $V(R)$ Eq. (26) is close to the real one. For large R it behaves as a polynomial in inverse powers of R, the exponential part falling to zero rapidly. Above $R\simeq 100$ (a.u.), the potential is

$$V(R)=-\frac{C_6}{R^6}-\frac{C_8}{R^8}-\frac{C_{10}}{R^{10}}. \tag{28}$$

To integrate analytically the system of Eq. (11) as well as the second integral in Eq. (13) is easy, consisting only of elementary operations. We have calculated these using MAPLE, which is able to give also an optimized FORTRAN

TABLE I. The scattering length a and effective range r_0 in a.u. at different values of the cutoff radius R_c.

R_c (a.u.)	a^{a}	a^{b}	a^{c}	r_0
23.215	376	352.5	350.630 5	169.984 3
23.190	140	144.2	145.433 6	157.589 4
23.165	65	68.0	68.215 96	624.553 3
23.140	−69	−67.7	−72.243 05	2069.113
23.115	467	485.3	477.146 5	1916.246

[a]Obtained by extrapolation procedure.
[b]Obtained by semiclassical procedure.
[c]Present calculation.

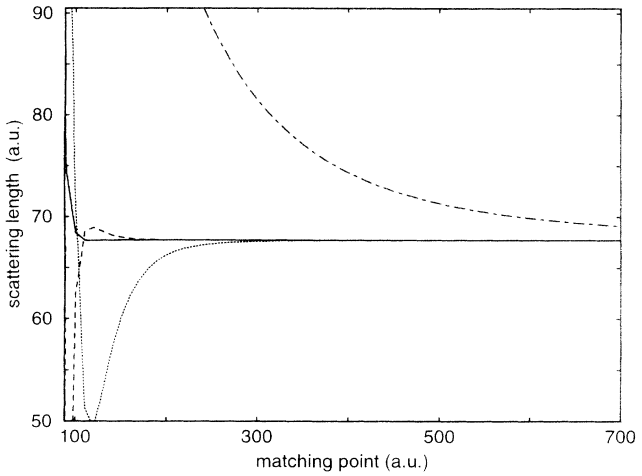

FIG. 1. The scattering length, $a^{(0)}$ dot-dashed line, $a^{(1)}$ dot line, $a^{(2)}$ dashed line, and $a^{(3)}$ solid line computed at different values of the matching point R_0.

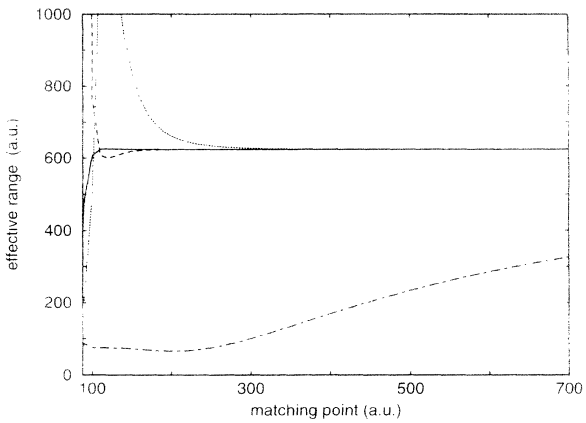

FIG. 2. The effective range, $r_0^{(0)}$ dot-dashed line, $r_0^{(1)}$ dot line, $r_0^{(2)}$ dashed line, and $r_0^{(3)}$ solid line computed at different values of the matching point R_0.

or C code for these quantities.

In Fig. 1 we display the value of scattering length $a^{(k)}$ for $k=0$, 1, 2, 3, computed at different values of the matching point R_0. Our intention was to compute the scattering length exact to seven digits and to find the smallest value of R_0 where this is achieved.

For R_0 bigger than a certain value, an important feedback is provided by the facts that $a^{(0)}(R_0)$ and $a^{(2)}(R_0)$ are decreasing functions of R_0 and $a^{(1)}(R_0)$ and $a^{(3)}(R_0)$ are increasing function of R_0, according to the conclusions of the previous section. Further for a given value of R_0 the exact value of the scattering length is bounded between $a^{(k)}$ and $a^{(k+1)}$ where $k=0,1,2$.

For the cutoff radius $R_c=23.165$ (a.u.) the scattering length has the value 68.215 96 (a.u.), exact to seven digits. This was obtained by $a^{(3)}$ at $R_0 \geq 250$ (a.u.), by $a^{(2)}$ at $R_0 \geq 480$ (a.u.), and by $a^{(1)}$ at $R_0 \geq 1270$ (a.u.). For $a^{(0)}$ this value is obtained at $R_0 \geq 40\,000$ (a.u.). As we can see, the δ corrections improve dramatically the performance of the computation in terms of time and precision.

The same discussion holds for the effective range. The results are presented in Fig. 2 for a cutoff radius $R_c=23.165$ (a.u.). In this case the contributions of the δ corrections are more important and improve the value of the second integral in Eq. (13). Actually $r_0^{(0)}$ represents the computation of the effective range in the absence of this integral. As Fig. 2 show, the contribution of this integral can not be ignored. It represents the area occupied by the difference between the square of the asymptote and the square of the solution above the matching point R_0, which is very narrow and extends to infinity. A pure numerical calculation of this area may not be possible without significant errors and the only way to avoid such errors is by analytical methods, as in Eq. (13).

Table I presents the values of the scattering length and effective range for different values of the cutoff radius R_c. Together with them are listed the values for scattering length obtained by Gribakin and Flambaum [3], using the extrapolation of the s wave phase shift towards zero energy, and a semiclassical approximation. Table I shows that the semiclassical approximation gives a better estimate than the extrapolation procedure. In the extrapolation procedure there are two sources of errors. One is related to the asymptotic behavior of the wave functions at very small energy which is reached only at very large R [5] and the second is the extrapolation itself which cannot guarantee any limits to the errors. In our approach there are no such difficulties. The numerical integration is done along a relative small range of R and the precisions of computation is guaranteed by the presence of the upper and lower limits. The results for different R_c demonstrate the extraordinary sensitivity of the scattering length a and effective range r_0 to the interatomic potential.

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