

Effective-Range Theory for van der Waals Scattering

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The $L > 0$ phase shifts δ_L for low-energy scattering by a van der Waals r^{-6} potential are calculated using the two-potential formula of scattering theory. We calculate $\tan\delta_L$ up to and including the $k^{2L+5} \ln k$ term. We compare our results with those obtained using the Born approximation.

I. INTRODUCTION

It is well known that the van der Waals r^{-6} potential appears as the dominant long-range attraction in atom-atom collisions. It also arises in electron-atom scattering as a correction to the static dipole polarizability r^{-4} potential, and has its origins in both the static quadrupole polarizability of the atom and the dynamical response of the atom to the incident electron.¹

The purpose of this paper is to present a derivation of an effective-range expansion for the van der Waals potential. Following Hinckelmann and Spruch,² we consider a scattering potential which consists of a short-ranged part $V(r)$ and a long-ranged part $U(r)$ such that

$$\begin{aligned} V(r) &= 0 \text{ for } r > d, \\ U(r) &= 0 \text{ for } r < d. \end{aligned} \quad (1)$$

Since $V(r)$ is short ranged, the scattering-phase shift from $V(r)$ is given by conventional effective-range theory:

$$\tan\delta_{L_s} = -A_{L_s} k^{2L+1} - \frac{1}{2} r_{L_s} A_{L_s}^2 k^{2L+3} + O(k^{2L+5}). \quad (2)$$

Here L is the orbital-angular-momentum quantum number and δ_{L_s} , A_{L_s} , r_{L_s} are the phase shift, scattering length, and effective range, respectively, when the scattering potential is V alone. When the scattering potential is $U+V$, the phase shift, scattering length, and effective range will be denoted by δ_L , A_L , and r_L , respectively. Starting from the radial Schrödinger equation, Hinckelmann and Spruch² show that to first order in the long-range potential,

$$\begin{aligned} \tan\delta_L &= \tan\delta_{L_s} - k^{-1}(1 - \tan^2\delta_{L_s})I(L) + 2k^{-1}\tan\delta_{L_s}J(L) \\ &\quad - k^{-1}\tan^2\delta_{L_s}K(L) + O(U^2), \end{aligned} \quad (3)$$

where

$$I(L) = \int_d^\infty (kr)^2 j_L^2(kr) \bar{U}(r) dr, \quad (4)$$

$$J(L) = \int_d^\infty (kr)^2 j_L(kr) n_L(kr) \bar{U}(r) dr, \quad (5)$$

$$K(L) = \int_d^\infty (kr)^2 [j_L^2(kr) + n_L^2(kr)] \bar{U}(r) dr. \quad (6)$$

Here $j_L(kr)$, $n_L(kr)$ are the usual spherical Bessel

and Neumann functions, respectively, and $\bar{U} = (2m/\hbar^2)U$. The potential \bar{U} is a van der Waals attraction:

$$\bar{U}(r) = -\gamma^4 r^{-6}, \quad r > d \quad (7)$$

where γ characterizes the strength of the interaction, and has the dimensions of a length. Hinckelmann and Spruch have discussed s -wave van der Waals scattering based on the formula (3). In what follows we will discuss van der Waals scattering for the higher partial waves. Our results are presented in Sec. II. In Sec. III we compare our results with those obtained using the first Born approximation.

II. EFFECTIVE-RANGE EXPANSIONS

Basically, the determination of an effective-range expansion according to the formula (3) involves the evaluation of the integrals $I(L)$, $J(L)$, and $K(L)$.

A. Evaluation of $I(L)$ for $L > 0$

On inserting (7) into (4) and making the substitution $z = kr$, we obtain

$$I(L) = -\frac{1}{2} \pi \gamma^4 k^5 \int_{kd}^\infty z^{-5} J_{L+1/2}^2(z) dz. \quad (8)$$

The integral in (8) may be evaluated for $L > 1$ by dividing the range of integration into two parts, one part extending from zero to infinity, and the other from zero to kd . The integral with range zero to infinity may be evaluated using Eq. 6.574-2 of Ref. 3. We find

$$\int_0^\infty z^{-5} J_{L+1/2}^2(z) dz = 6h(L), \quad L > 1 \quad (9)$$

where

$$h(L) = [(2L+5)(2L+3)(2L+1)(2L-1)(2L-3)]^{-1}. \quad (10)$$

Equation (9) is only valid provided $L > 1$. In other words, the p wave must be treated separately from the higher partial waves. To evaluate the integral from zero to kd , we may use the power-series expansion for the square of a Bessel function (Eq. 5.4 of Ref. 4):

$$J_{L+1/2}^2(z) = \sum_{m=0}^{\infty} a_{Lm} z^{2L+2m+1}, \tag{11}$$

where

$$a_{Lm} = \frac{(-1)^m (2L+2m+1)!}{2^{2L+2m+1} (2L+m+1)! [\Gamma(L+m+\frac{3}{2})]^2 m!}. \tag{12}$$

It follows that

$$\int_0^{kd} z^{-5} J_{L+1/2}^2(z) dz = \sum_{m=0}^{\infty} \frac{a_{Lm}}{2L+2m-3} (kd)^{2L+2m-3}, \quad L > 1. \tag{13}$$

Combining (8), (9), and (13), we obtain the value of $I(L)$ for $L > 1$:

$$I(L > 1) = -\frac{1}{2} \pi \gamma^4 k^5 \times \left(6h(L) - \sum_{m=0}^{\infty} \frac{a_{Lm}}{2L+2m-3} (kd)^{2L+2m-3} \right). \tag{14}$$

Considering the case $L = 1$, we make the substitution $z = kr$ in Eq. (4) and use the fact that⁵

$$j_1(z) = \sin z/z^2 - \cos z/z, \tag{15}$$

thus obtaining

$$I(L = 1) = -\gamma^4 k^5 \int_{kd}^{\infty} (z^{-6} + z^{-8} \sin^2 z - z^{-7} \sin 2z - z^{-6} \sin^2 z) dz. \tag{16}$$

The last three integrals in (16) may be evaluated by integration by parts. After somewhat tedious but straightforward algebra, we obtain the following expansions:

$$I(L = 1) = -\gamma^4 k^5 \left(\frac{1}{5(kd)^5} + I'_1 - I'_2 - I'_3 \right), \tag{17}$$

where

$$I'_1 = \int_{kd}^{\infty} z^{-8} \sin^2 z dz = \frac{1}{5(kd)^5} - \frac{1}{9(kd)^3} + \frac{2}{45kd} - \frac{2\pi}{315} + \frac{kd}{315} - \frac{2(kd)^3}{42525} + O(k^5), \tag{18a}$$

$$I'_2 = \int_{kd}^{\infty} z^{-7} \sin 2z dz = \frac{2}{5(kd)^5} - \frac{4}{9(kd)^3} + \frac{4}{15kd} - \frac{2\pi}{45} + \frac{8kd}{315} - \frac{4(kd)^3}{8505} + O(k^5), \tag{18b}$$

$$I'_3 = \int_{kd}^{\infty} z^{-6} \sin^2 z dz = \frac{1}{3(kd)^3} - \frac{1}{3kd} + \frac{\pi}{15} - \frac{2kd}{45} + \frac{(kd)^3}{945} + O(k^5). \tag{18c}$$

Finally, we have

$$I(L = 1) = \gamma^4 \left(-\frac{k^4}{9d} + \frac{\pi k^5}{35} - \frac{dk^6}{45} + \frac{d^3 k^8}{1575} + O(k^{10}) \right). \tag{19}$$

B. Evaluation of $J(L)$ for $L > 0$

On inserting (7) in (5), and making the substitution $z = kr$, we obtain

$$J(L) = (-1)^{L-\frac{1}{2}} \pi \gamma^4 k^5 \int_{kd}^{\infty} z^{-5} J_{L+1/2}(z) J_{-L-1/2}(z) dz. \tag{20}$$

The integral in (20) may be evaluated by dividing the range of integration into two parts, one part extending from kd to 1, and the other from 1 to ∞ . To evaluate the integral with range kd to 1, we use the power series (Eq. 5.4 of Ref. 4)

$$J_{L+1/2}(z) J_{-L-1/2}(z) = \sum_{m=0}^{\infty} b_{Lm} z^{2m}, \tag{21}$$

where

$$b_{Lm} = \frac{(-1)^m (2m)!}{2^{2m} (m!)^2 \Gamma(L+m+\frac{3}{2}) \Gamma(-L+m+\frac{1}{2})}. \tag{22}$$

We note that

$$b_{L0} = [(-1)^L / \pi] [1 / (L + \frac{1}{2})], \tag{23a}$$

$$b_{L1} = [(-1)^L / \pi]^{\frac{1}{2}} g(L), \tag{23b}$$

$$b_{L2} = [(-1)^L / \pi] 12h(L). \tag{23c}$$

Here

$$g(L) = [(L + \frac{3}{2})(L + \frac{1}{2})(L - \frac{1}{2})]^{-1}, \tag{24}$$

and $h(L)$ is defined by (10). Using (21), Eq. (20) yields the following result:

$$J(L > 0) = (-1)^{L-\frac{1}{2}} \pi \gamma^4 k^5 \left(\frac{b_{L0}}{4(kd)^4} + \frac{b_{L1}}{2(kd)^2} - b_{L2} \ln |2kd| + B - \sum_{m=3}^{\infty} \frac{b_{Lm}}{2m-4} (kd)^{2m-4} \right), \tag{25}$$

where

$$B = \int_1^{\infty} z^{-5} J_{L+1/2}(z) J_{-L-1/2}(z) dz - \frac{1}{4} b_{L0} - \frac{1}{2} b_{L1} + b_{L2} \ln 2 + \sum_{m=3}^{\infty} \frac{b_{Lm}}{2m-4}. \tag{26}$$

We note that B is independent of k . Inserting (23a)-(23c) in (25), we obtain the result

$$J(L > 0) = \gamma^4 \left(\frac{k}{4(2L+1)d^4} + \frac{g(L)k^3}{8d^2} - 6h(L)k^5 \ln |2kd| + O(k^5) \right). \tag{27}$$

C. Evaluation of $K(L)$ for $L > 0$

In order to evaluate the integral $K(L)$, we insert (7) in (6) and make the substitution $z = kr$, which gives

$$K(L > 0) = -\frac{1}{2} \pi \gamma^4 k^5 \int_{kd}^{\infty} z^{-5} [J_{L+1/2}^2(z) + J_{-L-1/2}^2(z)] dz. \tag{28}$$

The integral in (28) may be evaluated with the aid

of the identity (Eq. 9.62 of Ref. 4)

$$J_{L+1/2}^2(z) + J_{L-1/2}^2(z) = \frac{2}{\pi z} \sum_{m=0}^L c_{Lm} z^{2m-2L}, \quad (29)$$

where the coefficients c_{Lm} are given by

$$c_{Lm} = \frac{2^{2m-2L} (2L-m)! (2L-2m)!}{[(L-m)!]^2 m!}. \quad (30)$$

From (28) and (29), we obtain

$$K(L > 0) = \frac{\gamma^4}{d^5} \sum_{m=0}^L c_{Lm} \frac{(kd)^{2m-2L}}{2m-2L-5}. \quad (31)$$

It is now possible to calculate the phase shifts from Eq. (3). Inserting (2), (19), (27), and (31) into (3), we obtain an effective-range expansion for the p wave:

$$\tan \delta_1 = -A_1 k^3 - \frac{1}{35} \pi \gamma^4 k^4 - \frac{1}{2} r_1 A_1^2 k^5 - \frac{4}{35} \gamma^4 A_1 k^7 \ln |2kd| + O(k^7), \quad (32)$$

where

$$A_1 = A_{1s} + \gamma^4 \Delta, \quad (33a)$$

$$\Delta = -\left(\frac{1}{7} A_{1s}^2 - \frac{1}{6} A_{1s} d^3 + \frac{1}{9} d^6\right)/d^7, \quad (33b)$$

$$r_1 A_1^2 = r_{1s} A_{1s}^2 + \gamma^4 \delta, \quad (33c)$$

$$\delta = -\left(\frac{2}{45} d^8 - \frac{4}{15} A_{1s} d^5 - \frac{1}{6} r_{1s} A_{1s}^2 d^3 + \frac{2}{5} A_{1s}^2 d^2 + \frac{2}{7} r_{1s} A_{1s}^3\right)/d^7. \quad (33d)$$

Inserting (2), (14), (27), and (31) into (3), we obtain an effective-range expansion for the higher partial waves:

$$\tan \delta_L = 3\pi \gamma^4 h(L) k^4 - A_L k^{2L+1} - \frac{1}{2} r_L A_L^2 k^{2L+3} + 12\gamma^4 A_L h(L) k^{2L+5} \ln |2kd| + O(k^{2L+5}), \quad L > 1 \quad (34)$$

where

$$A_L = A_{Ls} + \gamma^4 \Delta', \quad (35a)$$

$$\Delta' = \frac{\pi d^{2L-3}}{2^{2L+2} (2L-3) [\Gamma(L + \frac{3}{2})]^2} + \frac{A_{Ls}}{2(2L+1)d^4} - \frac{[(2L)!]^2 A_{Ls}^2}{2^{2L} (2L+5) (L!)^2 d^{2L+5}}, \quad (35b)$$

$$r_L A_L^2 = r_{Ls} A_{Ls}^2 + \gamma^4 \delta', \quad (35c)$$

$$\delta' = -\frac{\pi(2L+3)d^{2L-1}}{2^{2L+3} (2L-1) [\Gamma(L + \frac{5}{2})]^2} - \frac{(2L-1)(2L-2)! A_{Ls}^2}{2^{2L-3} (2L+3) [(L-1)!]^2 d^{2L+3}} - \frac{[(2L)!]^2 r_{Ls} A_{Ls}^3}{2^{2L-1} (2L+5) (L!)^2 d^{2L+5}} + \frac{A_{Ls} g(L)}{2d^2} + \frac{r_{Ls} A_{Ls}^2}{2(2L+1)d^4}. \quad (35d)$$

In Eqs. (32) and (34) the coefficient of $k^{2L+5} \ln k$ actually contains A_{Ls} rather than A_L , but the replacement of A_{Ls} by A_L is legitimate since the error introduced is of second order in the long-range potential. For the p wave, Eq. (32) shows that the dominant term in the expansion of $\tan \delta_1$ at low energy exhibits a k^{2L+1} dependence, which is characteristic of short-ranged forces. The expansion of $\tan \delta_1$ also contains a higher-order logarithmic term $k^7 \ln k$, which is a consequence of the long-ranged nature of the potential. For the higher partial waves, Eq. (34) shows that $\tan \delta_L$ varies as k^4 at low energy. The expansion for $\tan \delta_L$ ($L > 1$) also contains a higher-order logarithmic term $k^{2L+5} \ln k$. The expansions (32) and (34) combine the characteristics of short-ranged potentials [i.e., they contain effective-range terms of the form given by Eq. (2)], with the characteristics of long-ranged potentials (i.e., they contain a k^4 term and a logarithmic term $k^{2L+5} \ln k$). Corresponding studies with a polarization r^{-4} potential have yielded results with the same general features.²

III. COMPARISON WITH BORN APPROXIMATION

van der Waals scattering has been discussed in the Born approximation in a previous article.⁶ Since the s -wave scattering has been previously discussed using the present approach² and using the Born approximation,⁶ we do not include this case in the discussion which follows.

In Ref. 6 we calculated the low-energy phase shifts for the potential

$$\bar{U}(r) = -\gamma^4 (r^2 + b^2)^{-3}, \quad r \geq 0 \quad (36)$$

using the first Born approximation. This potential asymptotically approaches the potential (7) of the present paper. It was found that for the p wave,

$$\tan \delta_1 = \frac{\pi \gamma^4 k^3}{48b} + O(k^4), \quad (37)$$

while for the higher partial waves,

$$\tan \delta_L = 3\pi \gamma^4 h(L) k^4 + O(k^5), \quad L > 1 \quad (38)$$

where $h(L)$ is given by Eq. (10).

A comparison between (37) and (32) shows that in the low-energy limit, $\tan \delta_1$ has the same dependence on k (viz., k^3) in the Born approximation as in the Schrödinger approach. While the effective-range expansion (32) contains higher-order logarithmic terms, the Born series (37) does not contain any logarithmic terms. For the higher partial waves, the dominant term in the effective-range expansion (34) and the dominant term in the Born series (38) are identically equal. As in the case of the p wave, the effective-range expansion (34) contains higher-order logarithmic terms which are not present in Born series (38). We conclude that at sufficiently low energies, and for partial waves higher than the

p wave, the Born approximation yields the same phase shifts as those obtained from a Schrödinger analysis.

We have just noted the substantial agreement between the Born approximation and Schrödinger theory for the case of van der Waals scattering. The fact that the Born approximation works so well for

long-range forces has been discussed in previous articles.^{7,8} Basically, the long-range forces give additional contributions precisely because of their long-range character; but at long ranges the potentials are arbitrarily weak, and therefore the leading terms are obtained exactly in the Born approximation, just as found above.

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Ionization of K Atoms in Collision with H₂, N₂, O₂, and CO[†]

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Absolute cross sections are reported here for the ionization of K atoms having laboratory energies in the range 20–1000 eV when interacting with H₂, N₂, O₂, and CO molecules. The range of energies covered, E , and the corresponding cross sections σ_{01} for each of the four target species are as follows: for O₂, $20 < E < 1000$ eV, $8 \times 10^{-19} < \sigma_{01} < 1.1 \times 10^{-15}$ cm²; for N₂, $50 < E < 1000$ eV, $2.5 \times 10^{-19} < \sigma_{01} < 4 \times 10^{-17}$ cm²; for CO, $100 < E < 1000$ eV, $2 \times 10^{-19} < \sigma_{01} < 2.3 \times 10^{-17}$ cm²; for H₂, $150 < E < 1000$ eV, $6 \times 10^{-20} < \sigma_{01} < 8 \times 10^{-18}$ cm².

I. INTRODUCTION

This paper describes the measurement of the absolute cross sections for ionization of K atoms on impact with diatomic atmospheric constituents. The cross sections are presented as a function of K-atom velocity from near threshold for the reaction to 1000 eV. From conservation of energy and momentum considerations, the threshold energy E_0 in the laboratory system for the ionization process is

$$E_i = M_1 E_0 / (M_1 + M_2), \quad (1)$$

where E_i is the amount of energy required to ionize potassium (4.3 eV) and M_1 and M_2 are the respective masses of the target molecules and potassium projectile atoms.

There are a number of reasons for choosing the alkali metals for the projectile atoms. The alkali-metal atoms are, in the first approximation, hydrogenic and therefore perhaps more amenable to analysis than other species. The fact that they are condensable made it possible to build a charge-transfer-type fast-atom accelerator which has little

or no slow-atom contamination in the beam. The alkali-metal atoms have large resonant charge-transfer cross sections, and they can be detected using surface ionization techniques. The choice of potassium for the initial measurements is appropriate because to date it is the only alkali-metal atom whose surface ionization behavior has been investigated as a function of energy for the range 0–1000 eV.^{1–3} There exist a number of recent measurements of low-energy ionization cross sections involving neutral targets and projectiles in the range from threshold to a few hundred eV.^{4–14} However, very few of these include alkali-metal atoms. In particular, for the ionization reactions considered here, no previous data appear to exist below 150 eV. For H₂, N₂, and O₂ comparison is possible with the data of Bydin and Bukhteev¹⁴ which span the range from 150–2200 eV. In addition there are the higher-energy data of Kikiani *et al.*¹⁵ which go from 3 to 15 keV.

II. EXPERIMENTAL APPARATUS

A. Vacuum System

Figure 1 is a schematic of the over-all experi-