Binding energy and scattering length for diatomic systems

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Abstract
We discuss the relationship between scattering length and binding energy for a
diatomic system with long-range van der Waals interaction. The well-known
relation, $\epsilon_0 = -(\hbar^2/2\mu)(1/a_0)^2$, is generalized to much higher orders for the
s wave. Analytic results for the binding energies of p and higher angular
momentum states are also presented.

A least-bound state of a diatomic molecule, such as the least-bound s state or the least-bound
p state (for spin-aligned fermions), plays a fundamental role in cold-atom physics. It is the
dominant final state for the three-body recombination process (see, e.g. [1, 2]) that determines
the lifetime of a condensate. It is also the state in which large samples of long-range molecules
[3, 4] may be formed by taking advantage of a Feshbach resonance [5–16]. The understanding
of the properties of this state, such as its energy, and how they relate to the scattering length,
is both useful experimentally and a necessary ingredient of any theoretical formulation.

While the binding energy may be easily computed numerically, such results are difficult to
use by experimentalists, and of little use in theoretical formulations for three- and many-atom
systems. Analytically, little is known about the binding energy of a diatomic molecule except
for the effective-range result of $\epsilon_0 = -(\hbar^2/2\mu)(1/a_0)^2$, which relates the s wave binding
energy to the s wave scattering length [17, 18]. This relation is, however, not applicable to any
other partial waves, because for atoms with long-range van der Waals interaction, the effective
range is not defined for the p wave and the scattering length has no definition for d and higher
partial waves [19, 20]. Even for the s wave, it is applicable only for very large scattering
lengths.

The angular-momentum-insensitive quantum defect theory (AQDT) [21–23] provides
a systematic understanding of highly-excited molecular rovibrational states and cold-atom
collisions. Here we apply it specifically to the binding energy of the least-bound state of an
arbitrary angular momentum l and derive simple analytic results that are easily accessible.
In particular, a new analytic representation of the s wave binding energy is presented that is
applicable over a much wider range of s wave scattering lengths than the effective-range result.
Similar representations of binding energies are also developed for p and higher partial waves

where no previous analytic results exist. (This is not surprising as no such results would have been possible without the analytic solution for the van der Waals potential [24].)

In AQDT, the bound spectra of a diatomic molecule with $-C_n/r^n$ long-range interaction are given rigorously by the solutions of [20, 21]

$$\chi_l^{c(n)}(\epsilon_s) = K^c(\epsilon, l). \tag{1}$$

Here the $\chi_l^{c(n)}$ function is a universal function that depends only on the exponent of the long-range interaction n and on the angular momentum l. The strength of the long-range interaction determines the energy scaling through the length scale $\beta_n = (2\mu C_n/\hbar^2)^{1/(n-2)}$,

$$\epsilon_s = \frac{\epsilon}{(\hbar^2/2\mu)(1/\beta_n^2)}. \tag{2}$$

For $n = 6$ that we are concerned with here [21],

$$\chi_l^{c(6)} = \frac{\tan\theta_l + \tan(\pi\nu/2)(1 + M_l)/(1 - M_l)}{1 - \tan\theta_l \tan(\pi\nu/2)(1 + M_l)/(1 - M_l)}, \tag{3}$$

in which $\tan\theta_l = Y_l/X_l$, $M_l = G_{\epsilon_s l}(-\nu)/G_{\epsilon_s l}(\nu)$, with ν, X_l, Y_l and $G_{\epsilon_s l}$, all of which are functions of the scaled energy ϵ_s, being given in [24].

Equation (1) is exact and applicable to all quantum systems with $V(r) \to -C_n/r^n$ at large distances. All the short-range physics is encapsulated in the short-range K matrix $K^c(\epsilon, l)$ [21, 23], or sometimes more conveniently, in the quantum defect $\mu^c(\epsilon, l)$ [23], which is defined to have a range of $0 \leqslant \mu^c < 1$ and be related, for $n = 6$, to K^c by

$$K^c(\epsilon, l) = \tan[\pi\mu^c(\epsilon, l) + \pi/8]. \tag{4}$$

Like $K^c(\epsilon, l)$, the quantum defect $\mu^c(\epsilon, l)$ depends only weakly on both the energy and the angular momentum l [23]. Its value at $\epsilon = 0$ and $l = 0$ is related rigorously to the s wave scattering length by ($n = 6$) [23]

$$\tan\pi\mu^c(0, 0) = \bar{a}_{0s}/(a_{0s} - \bar{a}_{0s}). \tag{5}$$

Here $a_{0s} = a_0/\beta_6$ is the scaled s wave scattering length, and

$$\bar{a}_{0s} = \frac{2\pi}{[\Gamma(1/4)]^2} = 0.477\,9888, \tag{6}$$

is the mean s wave scattering length of Gribakin and Flambaum [25], scaled by β_6.

As discussed in [23], the most convenient expansion parameter for describing a state of angular momentum l close to the threshold is $x_l(\epsilon)$, defined for $n = 6$ by

$$x_l(\epsilon) \equiv \tan[\pi\mu^c(\epsilon, l) - l\pi/4]. \tag{7}$$

With this definition, $x_l(0) = 0$ corresponds to having a bound or quasi-bound state of angular momentum l right at the threshold, while a small and positive $x_l(0)$ corresponds to having a bound state of l close to the threshold [22, 23].

For small energies around the threshold, the quantities in equation (3) can be represented by their respective expansions that derive straightforwardly from the results of [24]

$$\nu = \nu_0 - \frac{3}{2^5\nu_2(\nu_2^2 - 1)(\nu_2^2 - 4)}\epsilon_s^2 + O(\epsilon_s^4), \tag{8}$$

$$\tan\theta_l = -\frac{1}{2^2(\nu_2^2 - 1)}\epsilon_s + O(\epsilon_s^3), \tag{9}$$

$$M_l = (-1)^l \frac{\pi^2}{2^{4\nu_2 - 1}\sin(\pi\nu_0)} \frac{1}{[\Gamma(\nu_0)\Gamma(\nu_2 + 1)]^2}|\epsilon_s|^{\nu_2} + O(|\epsilon_s|^{\nu_2 + 2}\ln|\epsilon_s|), \tag{10}$$

where $\nu_0 = l/2 + 1/4$ and $\nu_2 = 2\nu_0 = l + 1/2$. Similar expansions were also used in deriving the generalized effective-range expansion of [20].

With $\chi_l^{c(6)}$ given by equations (3) and (8)–(10), equation (1) can be solved analytically in terms of x_l. For the s wave, we obtain

$$\epsilon_{0s} = -\frac{1}{\bar{a}_{0s}^2} x_0^2 \left[1 + g_1 x_0 + g_2 x_0^2\right] + O\left(x_0^5\right), \tag{11}$$

where ϵ_{0s} is the energy of an s wave bound state scaled according to equation (2), $x_0(\epsilon) = \tan[\pi \mu^c(\epsilon, 0)]$, and

$$g_1 = 2\left(\frac{1}{3\bar{a}_{0s}^2} - 1\right) = 0.917\,9195, \tag{12}$$

$$g_2 = (5/4)g_1^2 - 2 = -0.946\,7798. \tag{13}$$

We call equation (11) the generic expansion for the s wave. It is an exact expansion to the order of x_0^4 with no other assumptions or approximations. It is applicable even when $\mu^c(\epsilon, 0)$, and therefore $x_0(\epsilon)$, has substantial energy dependence over the range of $[\epsilon_0, 0]$. In practice, however, since we are looking only at a small range of energies covering the least-bound state, the energy dependence of $\mu^c(\epsilon, 0)$, and therefore $x_0(\epsilon)$, is completely negligible [21]. And this is true even when the short length scales become comparable to β_6 and the resulting potential supports only a few bound states [26]. Ignoring the energy dependence of μ^c, equation (11) gives the s wave binding energy in terms of the small parameter $\mu^c(0, 0)$, reflecting the fact that for $l = 4j$ (j being a non-negative integer), a small and positive $\mu^c(0, l)$ corresponds to having a bound state of l close to the threshold [22, 23].

Since $x_0(0) = \tan \pi \mu^c(0, 0)$ is related rigorously to the scattering length by equation (5), equation (11), with energy dependence of μ^c ignored, is exactly equivalent to the following expansion in $1/(a_{0s} - \bar{a}_{0s})$, consistent with the fact that a large, and positive, s wave scattering length corresponds to having a s wave bound state close to the threshold.

$$\epsilon_{0s} = -\frac{1}{(a_{0s} - \bar{a}_{0s})^2}\left[1 + \frac{c_1}{(a_{0s} - \bar{a}_{0s})} + \frac{c_2}{(a_{0s} - \bar{a}_{0s})^2}\right], \tag{14}$$

where

$$c_1 = \bar{a}_{0s}g_1 = 0.438\,7552, \tag{15}$$

$$c_2 = \bar{a}_{0s}^2 g_2 = -0.216\,3139. \tag{16}$$

Figure 1 compares this result, and the conventional effective-range result of $\epsilon_{0s} = -1/a_{0s}^2$, with the basically exact result given by AQDT. It is clear that equation (14) provides a much better approximation over a much wider range of scattering lengths. Note that it is very important to leave equation (14) as an expansion in $1/(a_{0s} - \bar{a}_{0s})$, instead of rewriting it in $1/a_{0s}$. Equation (14) is applicable over a wide range of scattering lengths where a_{0s} is not necessarily much greater than $\bar{a}_{0s}$. In fact, figure 1 shows it to be an excellent approximation for all $a_{0s} > 2\bar{a}_{0s}$, namely for all Class 0 systems according to the classification of [23]. Rewriting it as an expansion to the fourth order in $1/a_{0s}$ would destroy its accuracy and range of applicability. In other words, equation (14) is equivalent to much higher orders in $1/a_{0s}$ than $1/a_{0s}^4$; it is an entirely different expansion.

For the p wave, the solution of equation (1) with expansions, equations (8)–(10), gives

$$\epsilon_{1s} = -5x_1\left[1 + h_1 x_1^{1/2} + h_2 x_1\right] + O\left(x_1^{5/2}\right), \tag{17}$$
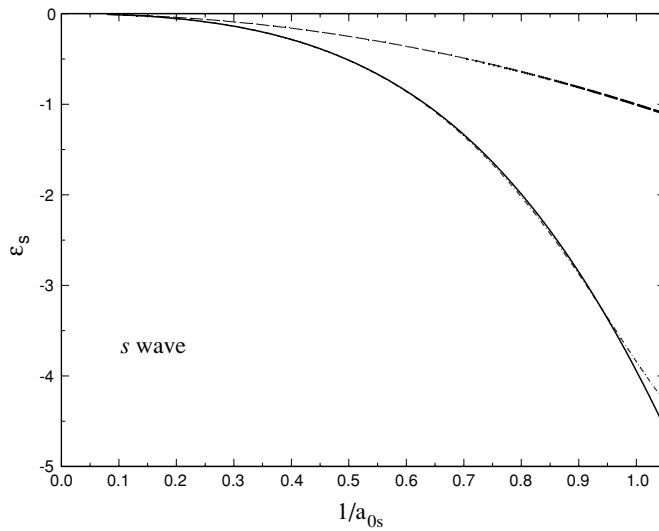
Figure 1. The s wave binding energy as a function of $1/a_{0s} = \beta_6/a_0$. Solid line: exact AQDT result. Dashed line: effective-range theory. Dash-dot line: result of the analytic representation, equation (14).

where ϵ_{1s} is the energy of a p wave bound state scaled according to equation (2), $x_1 = \tan \pi [\mu^c(\epsilon, 1) - 1/4]$, and

$$h_1 = \frac{5^{3/2}[\Gamma(1/4)]^2}{36\pi} = 1.299\,466,$$ (18)

$$h_2 = 3h_1^2/2 - 5\pi/14 = 1.410\,919.$$ (19)

Ignoring the energy dependence of μ^c, equation (17) gives the binding energy in terms of the small parameter $\mu^c(0, 1) - 1/4$, reflecting the fact that for $l = 4j + 1$ (j being a non-negative integer), a small and positive $\mu^c(0, l) - 1/4$ corresponds to having a bound state of l close to the threshold [22, 23].

For the p wave, the scattering length is also defined and is related to x_1 rigorously by equation (10) of [20] (in which $K_{l=1}^0$ is simply related to x_1 by $K_{l=1}^0 = -x_1$ [23])

$$x_1(0) = \left\{ \frac{36\pi}{[\Gamma(1/4)]^2} a_{1s} + 1 \right\}^{-1},$$ (20)

where $a_{1s} = a_1/\beta_6^3$ is the scaled p wave scattering length. Defining

$$\bar{a}_{1s} = \frac{[\Gamma(1/4)]^2}{36\pi} = 0.116\,2277,$$ (21)

equation (17), with the energy dependence of μ^c ignored, is exactly equivalent to

$$\epsilon_{1s} = -5\bar{a}_{1s} \left(\frac{1}{a_{1s} + \bar{a}_{1s}} \right) \left[1 + d_1 \left(\frac{1}{a_{1s} + \bar{a}_{1s}} \right)^{1/2} + d_2 \left(\frac{1}{a_{1s} + \bar{a}_{1s}} \right) \right],$$ (22)

where

$$d_1 = h_1 \bar{a}_{1s}^{1/2} = 0.443\,0163,$$ (23)

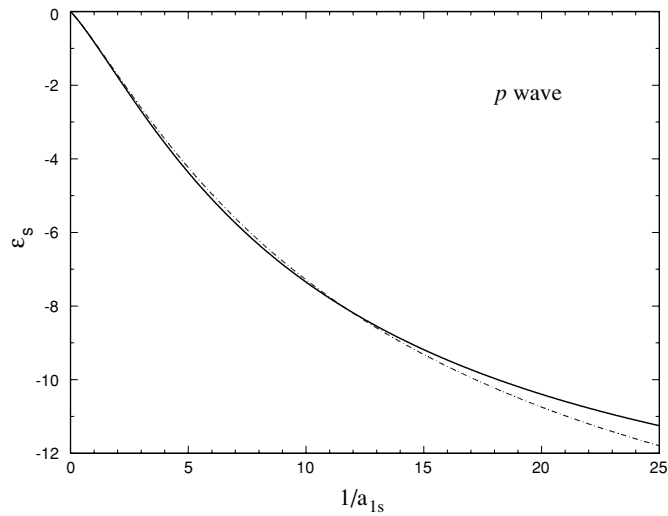$$d_2 = h_2 \bar{a}_{1s} = 0.163\,9879.$$ (24)

Figure 2. The p wave binding energy as a function of $1/a_{1s} = \beta_6^3/a_1$. Solid line: exact AQDT result. Dash-dot line: result of the analytic representation, equation (22).

Note that unlike the case of the s wave where the binding energy depends on $1/a_{0s}$ quadratically in the limit of large scattering length, the p wave binding energy depends on $1/a_{1s}$ linearly in the limit of $a_{1s} \to \infty$. Figure 2 shows that equation (22) provides an excellent approximation to the exact AQDT result over a wide range of energies and p wave scattering lengths. In fact, it is good approximation for almost all positive p wave scattering lengths except for a small region around $a_{1s} = 0$. (It covers virtually the entire region of Class 1, in the classification of [23].) Again, it is very important to leave equation (22) as an expansion in $1/(a_{1s} + \bar{a}_{1s})$ to maintain its range of applicability. Putting it another way, if one had started out looking for an expansion in a different variable, such as $1/a_{1s}$, it is very unlikely that one would ever achieve an expansion that can cover the entire region of $a_{1s} > 0$.

If the p wave scattering length is not known explicitly, it can be derived from the s wave scattering length by taking advantage of the approximate l-independence of μ^c. This was left as an exercise in [23], and the answer is

$$a_{1s} = \frac{[\Gamma(1/4)]^2}{18\pi} \frac{a_{0s} - \bar{a}_{0s}}{2\bar{a}_{0s} - a_{0s}}. \tag{25}$$

Using this result in equation (22) leads to an expansion of the p wave binding energy in terms of the s wave scattering length: an expansion in $2\bar{a}_{0s} - a_{0s}$, to be precise. The physical meaning is clear. An s wave scattering length that is less than, but close to $2\bar{a}_{0s}$ corresponds to having bound states of $l = 4j + 1$ close to the threshold [22, 23]. The same expansion in $2\bar{a}_{0s} - a_{0s}$ can also be obtained by using in equation (17) the following more general result:

$$x_l(0) = (2\bar{a}_{0s} - a_{0s})/a_{0s}, \qquad l = 4j + 1, \tag{26}$$

which follows immediately from equations (5) and (7) assuming l-independence of μ^c. We do not write this expansion explicitly here to encourage the use of equation (17), or equivalently, equation (22), when possible, as they do not rely on the l-independence of μ^c.

For $l \geqslant 2$, the following generic expansion is obtained:

$$\epsilon_{ls} = -(2l + 3)(2l - 1)x_l \left[1 + \frac{3\pi(2l + 3)(2l - 1)}{2(2l + 5)(2l + 1)(2l - 3)} x_l \right], \tag{27}$$
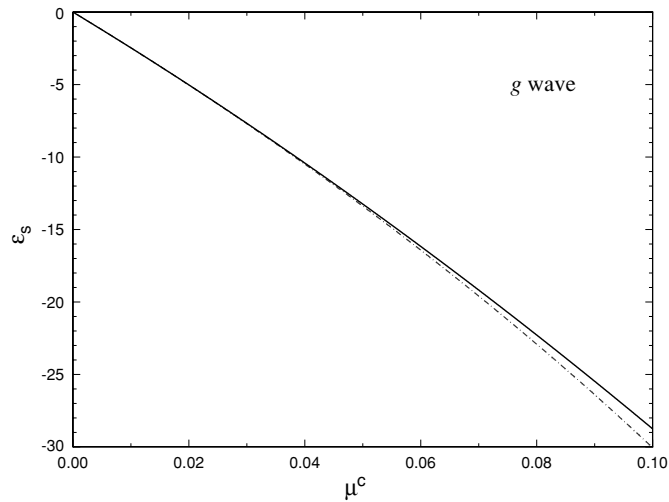
Figure 3. The g wave binding energy as a function of $\mu^c(0, 4)$. Solid line: exact AQDT result. Dash-dot line: the expansion to the order x_4^2, as given by equation (27).

where ϵ_{ls} is the energy of a bound state of angular momentum l scaled according to equation (2), and $x_l = \tan[\pi \mu^c(0, l) - \pi lb]$ ignoring the energy dependence of μ^c. This expansion works well over an ever greater range of scaled energies for larger l, because the expansions given by equations (8)–(10) are not only expansions in small ϵ_s, they are simultaneously expansions in large l [27]. Figure 3 shows the example of the g ($l = 4$) wave. The $l \geqslant 2$ partial waves have no well-defined scattering lengths and therefore no equivalents of equations (14) and (22).

If the value for $\mu^c(0, l)$ is unknown (it can in fact be easily computed exactly if needed [23]), it can again be derived from the s wave scattering length by utilizing the approximate l-independence of μ^c [21, 23]. In addition to equations (26), we have also from equations (5) and (7)

$$x_l(0) = \bar{a}_{0s}/(a_{0s} - \bar{a}_{0s}), \qquad l = 4j, \tag{28}$$

$$x_l(0) = (\bar{a}_{0s} - a_{0s})/\bar{a}_{0s}, \qquad l = 4j + 2, \tag{29}$$

$$x_l(0) = -a_{0s}/(2\bar{a}_{0s} - a_{0s}), \qquad l = 4j + 3. \tag{30}$$

Together they relate $x_l(0)$ to the s wave scattering length for all l. Using these results in equation (27) leads to corresponding expansions of ϵ_{ls} in terms of the s wave scattering length. For example, using equation (30) in equation (27) would lead to an expansion in a_{0s} for f and $l = 4j + 3$ partial waves, reflecting the physics that a small and negative a_{0s} corresponds to having a bound state of $l = 4j + 3$ close to the threshold [22, 23].

In conclusion, analytic representations for the binding energy of a least-bound state of any l have been derived at a number of different levels. For the generic expansions, the only error is the expansion error. Since we are looking only at the least-bound state, the energy variation of μ^c is negligible. The corresponding expansions, including the expansions in scattering lengths for both s and p partial waves and the generic expansions with the $\mu^c(\epsilon, l) \approx \mu^c(0, l)$ approximation, have essentially the same accuracy. Other expansions that make use of both the energy- and the l-independence of μ^c are examples of universal properties at length scale

β_6 [21, 23, 26, 28] described by a single parameter, be it $\mu^c(0, 0)$ or a_{0s}. They are very useful for qualitative understanding, and should also work well quantitatively for the first few partial waves. Conceptually and mathematically, the l-independence approximation does put a little stronger requirement on β_6 being longer than other length scales in the system, but it is a requirement that is well satisfied by virtually all real molecules [21, 23].

Finally, the derivation of the results offers an interesting example of functional representation in mathematical physics. Specifically, it shows that with a proper change of variable, a function that covers a wide range of one variable may be simply represented by a perturbative expansion in another. Physics, in this case AQDT [21–23], helps us to pick the right variable, in this case x_l, in which to do the perturbative expansion.

Acknowledgments

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