

## Critical binding of diatomic molecules

by J. LEKNER

Cavendish Laboratory, Cambridge

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The behaviour of two bodies that are just bound or nearly bound is discussed. A class of potentials is given for which Schrödinger's equation has exact solutions at critical binding (zero binding energy). This class includes the known solution for the 6-10 potential. For a general potential characterized by a coupling parameter  $\alpha$ , it is shown that the bound state energy tends to zero as  $-(\alpha - \alpha_0)^2$ , where  $\alpha_0$  is the critical value of the coupling parameter. Small energy scattering of atoms which are near critical binding (e.g. helium atoms) is examined. It is shown that determination of the total cross-section up to terms of order  $k^2$  is in principle sufficient to distinguish between bound and virtual states of the diatomic molecule.

### 1. INTRODUCTION

In this note we discuss certain properties of two-body systems which are near critical binding. The main practical interest lies in deciding whether or not two helium atoms bind to form a diatomic molecule, but the results obtained are general, and apply to any atomic or nuclear two-body problem where the interaction can be approximated by a central conservative field.

Consider two bodies, masses  $M_1$  and  $M_2$ , interacting with the potential  $U(r)$ . Let  $R(r)$  be the radial part of the wavefunction for zero orbital angular momentum, and  $\phi = rR$ . Then  $\phi$  satisfies the equation

$$\phi''(r) + \frac{2m}{\hbar^2} [E - U(r)]\phi(r) = 0, \quad (1)$$

where  $m^{-1} = M_1^{-1} + M_2^{-1}$ , and  $E$  is the energy of relative motion. In considering solutions of (1) it is convenient to express the potential as

$$U(r) = v u(r/a), \quad (2)$$

where  $v$  is a potential strength and  $a$  is a length. Well-known examples are the 6-12, 6-10 and Morse potentials :

$$U(r) = v \left\{ \left( \frac{a}{r} \right)^{12} - 2 \left( \frac{a}{r} \right)^6 \right\}, \quad (3)$$

$$U(r) = v \left\{ \frac{3}{2} \left( \frac{a}{r} \right)^{10} - \frac{5}{2} \left( \frac{a}{r} \right)^6 \right\}, \quad (4)$$

$$U(r) = v \left\{ \exp \left[ -2\beta \left( \frac{r}{a} - 1 \right) \right] - 2 \exp \left[ -\beta \left( \frac{r}{a} - 1 \right) \right] \right\}. \quad (5)$$

We have chosen the form of  $u$  so that each of these potentials attains its minimum value of  $-v$  at  $r = a$ . Any given potential can be expressed in the form (2), but

not in a unique way. This lack of uniqueness is irrelevant here. Sometimes it is convenient to consider together a class of potentials by letting  $u$  depend on one or more dimensionless parameters. For example, the Morse potential (5) is parametrized by  $\beta$ , a ratio of lengths.

The point of expressing the potential in the form (2) is that we can change to the dimensionless variables  $x=r/a$ ,  $\epsilon=2ma^2E/\hbar^2$ , and the system is then characterized by a single dimensionless quantity, the coupling parameter  $\alpha$  :

$$\alpha = 2ma^2v/\hbar^2. \quad (6)$$

A similar procedure was used by de Boer [1] in the discussion of many-body systems ; the classical analogue is called the principle of corresponding states.

In terms of the dimensionless variables, Schrödinger's equation becomes

$$\phi''(x) + [\epsilon - \alpha u(x)]\phi(x) = 0. \quad (7)$$

If  $U(r)$  has an attractive part, there may be a range of values of the coupling parameter  $\alpha$  for which bound states ( $\epsilon < 0$ ,  $\phi(\infty) = 0$ ) exist. We will consider potentials which have bound states for large  $\alpha$  ((3), (4) and (5) are of this type) ; the three questions we will try to answer are : (i) what is the critical value  $\alpha_0$  below which no bound states exist ? ; (ii) how does  $\epsilon$  approach zero as  $\alpha$  tends to  $\alpha_0$  ? ; and (iii) does low-energy scattering enable us to distinguish between  $\alpha > \alpha_0$  and  $\alpha < \alpha_0$  ? These questions are considered in the next three sections.

## 2. CRITICAL BINDING : A CLASS OF EXACT SOLUTIONS

The critical value  $\alpha_0$  of the coupling parameter for which the solution is on the borderline between bound and free states ( $\epsilon = 0$ ,  $\phi_0(\infty) = \text{constant}$ ) can be determined for each potential shape  $u(x)$  by direct numerical solution of

$$\phi_0''(x) - \alpha_0 u(x)\phi_0(x) = 0. \quad (8)$$

For example, the 6-12 potential of equation (3) has the critical value  $\alpha_0 = 7.043$ . (A variational estimate of 7.047 obtained by the Kilpatricks [2] is a little higher than this, as it should be.)

Since inter-atomic and inter-nucleon potentials are mainly phenomenological, with parameters determined by fitting virial coefficients or scattering data, it is interesting to note that there exists a class of potentials for which  $\phi_0$  and  $\alpha_0$  can be obtained analytically. These can be obtained as follows : in (8) we write  $\phi_0 = \exp \chi$ , so that

$$\chi'' + (\chi')^2 = \alpha_0 u. \quad (9)$$

It follows that for any  $w(x)$ , the potential

$$u(x) = \frac{1}{\alpha_0} [w'(x) + w^2(x)] \quad (10)$$

has the solution (normalized to unity at infinity)

$$\phi_0(x) = \exp \left\{ - \int_x^\infty dx w(x) \right\}. \quad (11)$$

The constraints on  $w$  are that  $u(x)$  tend to zero at infinity and that

$$\int_x^\infty dx w(x)$$

diverge to infinity as  $x$  tends to zero at least as fast as  $-\log x$ . The critical value of the coupling parameter is determined by specifying the position of the minimum of  $u$ , and its minimum value. For example, functions of the form

$$\begin{aligned} w(x) &= f(x)/x^n, \\ w(x) &= g(x)/(\sinh \beta x)^n, \end{aligned}$$

where  $f$  and  $g$  tend to constants at the origin and  $n \geq 1$  will give soluble potentials. The simplest example is  $w = \gamma/x^n$  ( $n$  need not be an integer). For  $n > 1$  we can constrain  $u(x)$  to a minimum value of  $-1$  at  $x = 1$ ; the critical coupling parameter and the potential are then

$$\begin{aligned} \alpha_0 &= \frac{1}{4}(n^2 - 1), \\ u(x) &= \frac{1}{n-1} \left\{ \frac{n+1}{x^{2n}} - \frac{2n}{x^{n+1}} \right\}. \end{aligned} \quad (12)$$

The critically bound states are

$$\phi_0(x) = \exp \left\{ -\frac{1}{2} \left( \frac{n+1}{n-1} \right) x^{-n+1} \right\}. \quad (13)$$

This set includes the known analytic solution for the 6-10 potential [3-5].

The set of exact solutions obtained from a given  $w(x)$  may be enlarged in two ways: We note first that since  $\phi$  is to be zero at the origin and also at a point where the potential becomes infinite, a potential which is infinity for  $x < c$  and  $\alpha u(x-c)$  for  $x > c$  has wavefunction zero for  $x < c$  and  $\phi(x-c)$  for  $x > c$ . This result applies also to critically bound states, and thus the core-shifted potential has the same  $\alpha_0$  as the original potential.

The second method is best illustrated by an example: we set  $w = \gamma/(x-d)^n$ , where  $d < 1$ , and make the  $u(x)$  of equation (10) take its minimum value of  $-1$  at  $x = 1$ . We obtain (for  $n < 1$ )

$$\begin{aligned} \alpha_0 &= \frac{1}{4}(n^2 - 1)/(1-d)^2, \\ u(x) &= \frac{1}{n-1} \left\{ (n+1) \left( \frac{1-d}{x-d} \right)^{2n} - 2n \left( \frac{1-d}{x-d} \right)^{n+1} \right\}, \end{aligned} \quad (14)$$

and

$$\phi_0(x) = \exp \left\{ -\frac{1}{2} \left( \frac{n+1}{n-1} \right) \left( \frac{1-d}{x-d} \right)^{n-1} \right\} \quad (15)$$

for  $x > d$ . For  $x < d$   $u(x)$  is infinity and  $\phi_0(x)$  zero.

### 3. THE APPROACH TO CRITICAL BINDING

Potentials  $U(r)$  which have an absolute minimum  $-v$  have binding energy  $E = -v$  in the classical limit. Thus for large  $\alpha$ ,  $\epsilon$  tends to  $-\alpha$ . The semi-classical correction, proportional to  $\alpha^{1/2}$ , is obtained in the usual way by expanding

$u(x)$  about its minimum at  $x=1$  ; the eigenstates are approximately those of a harmonic oscillator, with lowest eigenvalue.

$$\epsilon \simeq -\alpha + [\alpha u''(1)/2]^{1/2}. \quad (16)$$

As  $\alpha$  decreases,  $|\epsilon|$  decreases, eventually becoming zero at  $\alpha = \alpha_0$ . We will show that  $\epsilon$  tends to zero as  $-(\alpha - \alpha_0)^2$ . This is contrary to simplest expectations : Mahan and Lapp [5] assume that the behaviour is linear in  $\alpha - \alpha_0$  (see their figure 1.) We multiply equation (7) by  $\phi_0$  and equation (8) by  $\phi$ , subtract, and integrate from zero to infinity. This gives

$$[\phi_0 \phi' - \phi_0' \phi]_0^\infty + \epsilon \int_0^\infty dx \phi_0 \phi = (\alpha - \alpha_0) \int_0^\infty dx u \phi_0 \phi. \quad (17)$$

Both  $\phi$ 's are zero at  $x=0$ . Outside the range of the potential,  $\phi_0$  is a constant, which we choose to be unity, and  $\phi$  goes to zero exponentially :

$$\phi \sim \exp[-(-\epsilon)^{1/2}x].$$

The first term in (17) is thus zero. In the second term, the integral

$$\int_0^\infty dx \phi_0 \phi$$

tends to  $(-\epsilon)^{-1/2} + \text{constant}$  as  $\alpha$  tends to  $\alpha_0$  (and  $\epsilon$  tends to zero). The integral on the right side has the limiting value

$$\int_0^\infty dx u \phi_0^2.$$

Thus we find

$$(-\epsilon)^{1/2} = -(\alpha - \alpha_0) \int_0^\infty dx u(x) \phi_0^2(x) \quad (18)$$

in the limit as  $\alpha \rightarrow \alpha_0$  from above. The integral on the right is negative definite, since it is proportional to the potential energy in the critically bound state, which is equal to minus the kinetic energy, the latter being positive definite :

$$\alpha_0 \int_0^\infty dx u \phi_0^2 + \int_0^\infty dx (\phi_0')^2 = 0. \quad (19)$$

Thus

$$\epsilon = -\frac{(\alpha - \alpha_0)^2}{\alpha_0^2} \left\{ \int_0^\infty dx (\phi_0')^2 \right\}^2. \quad (20)$$

We have thus determined the behaviour of  $\epsilon(\alpha)$  at both ends of the spectrum.

The above relations are for  $s$ -states. For bound states having angular momentum  $L$  the potential  $u(x)$  is replaced by

$$u_L(x) = u(x) + L(L+1)/x^2 \quad (21)$$

in equation (18), and (16) has to be modified by calculating the minimum and the second derivative at the minimum of the effective potential  $u_L(x)$ .

## 4. BOUND STATES, VIRTUAL STATES, AND LOW ENERGY SCATTERING

The question of whether two  $\text{He}^4$  atoms form a diatomic molecule or not is difficult to answer by the determination of  $\alpha$  for a given potential shape, and comparison with  $\alpha_0$ . The reason for this is that, for all potentials,  $\alpha$  lies close to  $\alpha_0$ , but the uncertainty is greater than  $|\alpha - \alpha_0|$ . For example, Feenberg [4] quotes three values of  $\alpha$  for the 6-12 potential determined by different authors in two different ways. The values are 6.94, 7.29 and 7.51 (for details see Feenberg, table II) ; the critical value of the coupling parameter is 7.04. Thus a  $(\text{He}^4)_2$  molecule exists according to the last two determinations, but not according to the first.

It may therefore be useful to have another way of distinguishing between bound and nearly bound (virtual) states, and if possible one which is independent of choice of potential. We will show that, in principle, one such method is the determination of the cross-section up to terms of order  $k^2$ . The approach used is similar to effective range theory, but using the critically bound state  $\phi_0$  instead of the free state as the reference wavefunction.

We consider solutions  $\phi(q, x)$  of equations (7) for small positive energies  $\epsilon = q^2$ , with  $\alpha$  near  $\alpha_0$ . We use the identity [cf. (17)]

$$[\phi_0\phi' - \phi_0'\phi]_0^x + q^2 \int_0^x dx \phi_0\phi = (\alpha - \alpha_0) \int_0^x dx u \phi_0\phi. \quad (22)$$

Let  $\rho$  be the range of the potential. For  $x > \rho$  we write  $\phi = \sin(qx + \delta)/\sin \delta$ , where  $\delta$  is the  $s$ -wave phase shift. We again normalize  $\phi_0$  to unity at infinity (i.e. for  $x > \rho$ ). The left side of (22) becomes, for  $x > \rho$ .

$$q \cos(qx + \delta)/\sin \delta + q^2 \int_0^\rho dx \phi_0\phi + q^2 \int_\rho^x dx \phi_0\phi.$$

For small energies  $\phi$  is equal to  $\phi_0$  plus a term of order  $\alpha - \alpha_0$  in the range of the first integral, while  $\phi_0$  is equal to unity in the range of the second integral. The left side thus reduces to

$$q^2 \int_0^\rho dx \phi_0^2 - q \sin q\rho + q \cos q\rho \cot \delta. \quad (23)$$

As  $q$  tends to zero, equation (22) thus gives

$$q \cot \delta = (\alpha - \alpha_0) \int_0^\infty dx u \phi_0^2 + q^2 \int_0^\infty dx (1 - \phi_0^2). \quad (24)$$

The terms omitted from (24) are of order  $(\alpha - \alpha_0)^2$  and  $q^2(\alpha - \alpha_0)$ . This expression is of the same form as that obtained by effective range theory [6] :

$$k \cot \delta = -s^{-1} + \frac{1}{2} r_0 k^2, \quad (25)$$

where  $s$  is the zero-energy scattering length,  $r_0$  the effective range, and  $k = q/a$  the wavenumber. We have thus shown that for a system near critical binding, the scattering length and effective range are given by

$$a/s = -(\alpha - \alpha_0) \int_0^\infty dx u \phi_0^2, \quad (26)$$

$$r_0/a = 2 \int_0^\infty dx (1 - \phi_0^2). \quad (27)$$

The first expression, together with the results of the previous section, gives

$$s = \pm \left( \frac{\hbar^2}{2m|E|} \right)^{1/2} = \pm \frac{a}{|\epsilon|^{1/2}}, \quad (28)$$

where the positive sign is to be taken for bound states ( $\epsilon < 0$ ), and the negative sign for virtual states. In both cases the  $\epsilon$  in equation (28) is understood to be given by equations (18) or (19). This result is well known [6, 7], but the derivation is new and shows explicitly the variation of  $s$  with  $\alpha$  near  $\alpha_0$ .

The total cross-section up to terms of order  $k^2$  is given by

$$\sigma = \frac{4\pi}{k^2 + k^2 \cot^2 \delta} = \frac{4\pi s^2}{1 + (ks)^2 [1 - r_0/s]}. \quad (29)$$

Thus by plotting  $\sigma^{-1}$  versus  $k^2$  one can determine the sign of  $r_0 s$ . We will see that, for potential shapes of interest,  $r_0$  is positive near critical binding, and therefore the sign of  $s$  (and thus of  $\alpha - \alpha_0$ ) can in principle be determined.

The effective range near critical binding is given by (27), with  $\phi_0$  normalized to unity at infinity. We consider potentials  $u(x)$  which are positive for  $x$  less than some  $x_0$ , and remain negative for  $x$  greater than  $x_0$ . Interatomic potentials are of this type. Then, from (7), the curvature of  $\phi_0$  is upward for  $x < x_0$  and downward for  $x > x_0$ . Since  $\phi_0(0) = 0$  and since  $\phi_0$ , being the limiting form of the lowest bound state, does not change sign, it follows that  $\phi_0$  increases monotonically up to its asymptotic value. Thus  $r_0$  is positive near critical binding. That it is not *always* positive is shown most simply by the counter-example  $u(x) = \delta(x - 1)$ , for which

$$\begin{aligned} \frac{s}{a} &= \frac{\alpha}{\alpha + 1}, \\ \frac{r_0}{a} &= \frac{2}{3} \frac{\alpha - 1}{\alpha}, \end{aligned} \quad (30)$$

The range of validity of (29) is  $ka \gtrsim 1$ . For He<sup>4</sup> atoms this means that the scattering cross-section has to be measured at velocities of about 50 m/s or less (corresponding to thermal velocities of about 1 K). The existence of a bound state is determined by the sign of  $s$  or  $r_0 s$ . From (29) we see that

$$\frac{r_0}{s} = 1 - \left\{ \frac{\sigma(0)}{\sigma(k)} - 1 \right\} / (ks)^2, \quad (31)$$

while from (26), (27) and (19) it follows that  $r_0/s$  is equal to  $(\alpha - \alpha_0)/\alpha_0$  times a numerical constant of order unity (equal to  $5\pi/4\sqrt{2}$  in the case of the 6–10 potential, for example). The right side of (31) has to be determined with sufficient accuracy to fix its sign. This demands that its uncertainty be less than its absolute magnitude, which is of order  $|\alpha - \alpha_0|/\alpha_0$ . The need is thus for data at speeds of 50 m/s or less, accurate enough for extrapolation of  $\sigma(k)$  to obtain  $\sigma(0)$ , and for the determination of the sign of the right side of (31). The latest experimental data for helium [8] is at slightly higher speeds, and with experimental uncertainties about three times greater than that needed, so that no conclusions can be drawn at present.

We note finally that equation (29) describes the scattering of two distinguishable particles. For identical Bose particles of zero spin (e.g. He<sup>4</sup> atoms), the appropriate low-energy cross-section is (29) multiplied by four ([7] §135). This effect has no influence on equation (31) or its consequences.

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