Quantum unbinding in potentials with $1/r^p$ tails

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Potentials with repulsive power behavior at large distances may or may not have a zero-energy bound state, depending only on the power p and, if $p = 2$, the strength. For the case of no zero-energy bound state, we further study how the state unbinds as the attractive, small r part of the potential is tuned to let the binding energy go to zero. Although motivated by the physics of wetting, this problem is well suited for senior or graduate level quantum mechanics courses by giving a novel perspective of solutions to one-dimensional Schroedinger equations.

I. INTRODUCTION

In a typical senior- or first-year graduate textbook[1,2] on nonrelativistic quantum mechanics one encounters a chapter on solving the one-dimensional Schroedinger equation with a variety of potentials. In addition to finding specific wavefunctions and energy eigenvalues associated with square wells and simple harmonic potentials, there would be some discussion of general properties such as the number of bound states and the distribution of their energies given certain qualitative features of any potential. The subject is quite old, so that new perspectives or problems, especially ones that are physically rather than mathematically motivated, are rarely seen. Recently, in connection with the phenomenon of wetting transitions,[3] such a novel problem appeared. Moreover, we believe it is sufficiently simple to be included in the typical course.

For potentials that vanish at large distances, one learns that positive/negative energy solutions correspond to unbound/bound states. The borderline case, a zero-energy solution, is more delicate and usually ignored. In this article, we will study this delicate threshold and be concerned with *how a state becomes unbound* if the (short distance parts of the) potential is changed so that a negative energy eigenvalue vanishes. Section II is devoted to setting up the problem and specifying the class of potentials and quantities to be used to define "unbinding." Section III contains the analysis. A summary of the results and a discussion of the origin and application of this study are found in the Sec. IV.

II. THE PROBLEM OF UNBINDING

Consider the Schroedinger equation for a particle with mass m in a central potential $V(r)$,

$$(- h^2/8\pi^2 m)\nabla^2\psi + V(r)\psi = E\psi. \tag{1}$$

Concentrating on the zero angular momentum solution, let us look at the radial equation for $R \equiv r\psi$. The problem is now one dimensional (on the semi-infinite interval $[0,\infty]$). Defining U and ϵ by $8\pi^2 m/h^2$ times V and $(-E)$, respectively, the equation now reads

$$R''(r) - U(r)R(r) = \epsilon R(r), \tag{2}$$

where $R'' \equiv (d^2 R/dr^2)$. Note that $\epsilon \geqslant 0$ for bound states.

In this article we study the class of U's that behave asymptotically, at large r, as

$$U(r) \to Ar^{-p}, \tag{3}$$

where A is a positive coefficient. These are therefore potentials with *repulsive tails*. Examples include the case of $p = 2$ for angular momentum barriers. The small r part of U is left unspecified except that it must contain some attractive components so that a bound state may exist. (See Fig. 1.)

Since $U(\infty) = 0$, the energy of this bound state cannot be positive. However, as we will demonstrate below, it may be zero under certain circumstances. If there is no zero-energy bound state, we may ask how the state unbinds as the energy is raised toward zero. One does not normally think of the bound state energy E as a control parameter; one normally thinks of the potential V as controllable. Here, we assume that the small r part of V can be tuned (without changing the asymptotic Ar^{-p} part) so that $E \to 0$.

To study quantitative aspects of unbinding we define two characteristic lengths, one associated with the energy (E or ϵ) and another associated with the wavefunction (ψ or R):

$$\lambda \equiv 1/\sqrt{\epsilon}; \tag{4}$$

$$l \equiv \left(\int r|R|^2 dr\right)\Big/\left(\int |R|^2 dr\right). \tag{5}$$

The physical meaning of λ is standard: for $r \gg \lambda$, R decays exponentially with r/λ. To be precise, this behavior really does not set in until values of r for which $U(r)\lambda^2 \ll 1$. Since we are interested in potentials with r^{-p} tails, this condition can be satisfied for sufficiently large r. To analyze unbinding, we consider the limit $\lambda \to \infty$, corresponding to $E \to 0$.

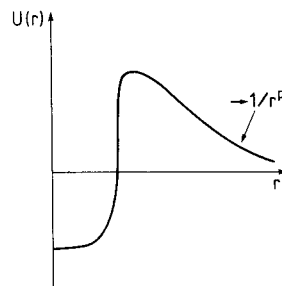The other length l is nothing but the expectation value of

Fig. 1. Sketch of a typical potential with short-range attraction and long-range repulsion.

r. Although the state is, by definition, bound if and only if ψ is normalizable, we find it convenient to use l for discussing unbinding. Having a physical dimension of length, it naturally characterizes the "size" of a bound state.[4] For $E < 0$, l would certainly be of the order of λ. As $E \to 0$, we expect l to diverge if a zero-energy bound state does not exist. If, on the other hand, the state remains bound as E vanishes, then l will typically be finite at $\lambda = \infty$. (Atypical cases will be discussed in detail later.) So l serves as a good parameter to measure "unbinding." An intuitive argument, based on the comments of the previous paragraph, would lead us to expect $l \propto \lambda$ as $\lambda \to \infty$. Another favorite argument of the physicist, dimensional analysis, also leads to the same conclusion:

$$l \to \lambda^q, \tag{6}$$

with $q = 1$.

This intuitive picture is largely confirmed except for a range of A in the $p = 2$ case, where the power q interpolates smoothly between 1 and 0 (the latter cooresponding to the bound case). Of course, one may use higher moments of r to measure "unbinding," a favorite being the root mean square deviation from the origin. For $p \neq 2$, the conclusions are unchanged. For $p = 2$, we will remark on the changes. The reader who abhors analytical details may skip to the results in Sec. IV.

III. HOW DOES A STATE UNBIND?

To find the quantitative aspects of unbinding, the general strategy will be as follows. For the distinct classes of p and A, we study the asymptotic behavior of the solutions to Eq. (2) with $\epsilon = 0$. Of the two solutions, we denote the one that is less singular at $r = \infty$ by R_0. Now, a state is certainly bound if l is finite. This is true if R_0 vanishes at large r with an inverse power greater than unity. Otherwise, l diverges and we consider the $\epsilon > 0$ ($E < 0$) solution, analyze its asymptotic behavior, and find how l diverges with λ. In addition, we will encounter the interesting possibility of a zero-energy bound state with diverging l.

Following standard routes, we define $f(r)$ by

$$R \equiv \exp(-f) \quad \text{or} \quad f \equiv -\ln(R), \tag{7}$$

so that Eq. (2) with $\epsilon = 0$ now reads

$$-f'' + (f')^2 = U. \tag{8}$$

Since $U \to Ar^{-p}$ for large r, the asymptotic behavior of f is also a power:

$$f \to r^s. \tag{9}$$

For convenience, we distinguish three cases: If $s < 0$, then the first term (f'') dominates in Eq. (8), if $s > 0$, then the second dominates, the $s = 0$ case is more delicate and will be studied separately.

These three cases correspond precisely to $p > 2$, $p < 2$, and $p = 2$, respectively.

A. Potential tails with $p > 2$

Here, $s = 2 - p$ is negative so that f vanishes at $r = \infty$. Thus R approaches a constant at large distances. Before we jump to the conclusion that a zero-energy bound state does not exist, we should inquire about the other solution. There are two solutions to a second-order differential equation such as (2); perhaps the other one is less "singular" at $r = \infty$. The other solution to (2), given by[5]

$R(r) \int^r dx [R(x)]^{-2}$, is more singular, approaching r instead of a constant. So, $R_0 \to$ constant and we conclude that there is no zero-energy bound state.

Next, we consider $\epsilon > 0$ solutions. How does R_0 behave now at large r? Again, the answer is standard. For $r \gg (A/\epsilon)^{1/p}$ (i.e., $U \ll \epsilon$), the bound state R_0 approaches $\exp(-r/\lambda)$. Apparently, then, as $\epsilon \to 0$ and $\lambda \to \infty$, this solution goes over to the one we found, i.e., $R_0 \to$ constant. It is now clear that the behavior of R_0 as $\lambda \to \infty$ is

$$R_0 \propto 1, \quad \text{for } \lambda \gg r \gg a, \tag{10a}$$

$$R_0 \propto e^{-r/\lambda}, \quad \text{for } r \gg \lambda, \tag{10b}$$

where a is some radius, outside which U is dominated by Eq. (3) only.

Proceeding to calculate the integrals in Eq. (5), we would have to find the details of the crossover from (10a) to (10b). This formidable task is, fortunately, not necessary since we are only interested in the divergent behavior of l as $\lambda \to \infty$. Although a rigorous proof may be presented, here we only state that it suffices to approximate R by R_0 for $r \ll \lambda$ and zero beyond that. The idea behind the approximation is simple: The exponential (10b) acts as a cutoff for R. The integrals in (5) are then trivial, leading to $l \propto \lambda$, i.e., $q = 1$.

B. Potential tails with $p < 2$

Here, the second term in Eq. (8) dominates so that $s = 1 - \frac{1}{2}p$ is positive and f diverges at $r = \infty$. Thus the less singular solution is given by $R_0 \to \exp(-r^s)$, giving us a zero-energy bound state. It is easy to see that l (as well as all the moments of R_0^2) is finite. It does not diverge with λ, a fact we characterize by $q = 0$.

C. Potential tails with $p = 2$

For this power, the amplitude A becomes dimensionless and Eq. (2) for R with $\epsilon = 0$ becomes trivially soluble by

$$R \propto r^\alpha, \tag{10}$$

provided $\alpha(\alpha - 1) = A$. Notice that the usual angular momentum barrier is a potential of this type. Although the full solutions, with $\lambda < \infty$, are known to be Bessel functions, we need only elementary functions for our arguments.

As before, we seek the less singular R_0, which would have

$$\alpha = \frac{1}{2}(1 - \sqrt{1 + 4A}). \tag{11}$$

Thus a zero-energy bound state exists if $\alpha < -\frac{1}{2}(A > \frac{3}{4})$. Unlike the case in Sec. III B, however, R_0 decays as a power of r. Thus it is possible to have infinite moments (e.g., l) for a zero-energy bound state.

We face five possibilities:

(1) If $\alpha < -1(A > 2)$, $\int r R_0^2$ converges and we have $q = 0$.

(2) For $\alpha = -1(A = 2)$, the divergence of $\int r R_0^2$ is logarithmic, i.e., $l \to \ln \lambda$.

(3) For $-1 < \alpha < -\frac{1}{2}, (2 > A > \frac{3}{4})$, l is infinite if $\lambda = \infty$. However, due to the finiteness of the denominator $\int R_0^2$ (in the limit $\lambda \to \infty$), the dependence on λ in l comes purely from the numerator $\int r R_0^2$. Using the same approximations discussed in Sec. III A, we obtain $l \propto \lambda^{2\alpha + 2}$, so that $q = 3 - \sqrt{1 + 4A}$.

(4) For $\alpha = -\frac{1}{2}(A = \frac{3}{4})$, it is $\int R_0^2$ that diverges logarithmically, leading to $l \to \lambda / \ln \lambda$.

(5) Finally, for $\alpha > -\frac{1}{2}(A < \frac{3}{4})$, both $\int r R_0^2$ and $\int R_0^2$ diverge if $\lambda = \infty$, so that the arguments presented in the case in Sec. III A apply again. We conclude that $q = 1$.
This ends our analysis of the divergent behavior of l.

We conclude this section by simply stating how these results change if we had chosen to consider the nth root of the nth moment with $n \neq 1$. Instead of 2, $(n + 1)(n + 3)/4$ will be the critical value of A, above which $q = 0$ and below which $q = 1 + (2 - \sqrt{1 + 4A})/n$. Clearly, $\frac{3}{4}$ is still the lower limit for A, below which $q \equiv 1$.

IV. SUMMARY AND CONCLUSION

We have studied quantum mechanical problems involving potentials that are *repulsive* at large distances but sufficiently attractive at small distances to support bound states. In particular, we considered repulsive tails of the form $A r^{-p}$, where A is a constant ("strength"), and asked whether, and how, a state unbinds as the small r part of the potential is tuned so that the binding energy $(-E)$ vanishes. Choosing to characterize the "boundedness" of the state by l, the expectation value of r, we found it convenient to describe the unbinding of a state by the power q in

$$l \propto (-E)^{-q/2}. \tag{15}$$

If this repulsive-tailed potential decays slowly enough ($p < 2$), it supports a zero-energy bound state and $q \equiv 0$. For $p > 2$ tails, no zero-energy bound state exists and $q \equiv 1$. For the delicate case of inverse square potentials q may depend on the strength A, interpolating between 0 and 1:

$$q = 3 - \sqrt{1 + 4A}, \tag{16}$$

for $2 > A > 3/4$. At the borderline values, l diverges with an additional logarithmic factor $\ln E$.

If we had chosen to describe unbinding by looking at the expectation value of some other power of r instead, the results remain unchanged for $p \neq 2$. However, for inverse square potentials, the interpolating $q(A)$ will differ somewhat; as will the upper borderline value of A.

Where do such strange potentials occur in nature? They appear as effective potentials for the interface coordinate in wetting transitions. We conclude this article with a brief discussion of the physics of wetting and the meaning of V and l in these transitions.

The simplest example of wetting is a liquid–gas system in the presence of a substrate, such as a container wall. Set the pressure and temperature (or some other control parameters) so that an infinite system would be in the gas phase, but near liquid–gas co-existence. If the liquid phase is preferentially adsorbed on the substrate, a thin film of liquid will condense out on it. As co-existence is approached, the thickness of this film may either grow without bound ("wetting" the substrate) or remain finite. It may happen that a portion of the line of two phase co-existence is nonwet but that at a certain point, called the wetting transition, the liquid will wet the substrate. The thickness of the adsorbed liquid layer exhibits a characteristic singular behavior as the transition point, labeled by T_W, is approached along the co-existence line from the nonwet portion. To study this transition, we describe the system by a fluctuating interface between the gas and the liquid and then perform a thermal average over these fluctuations. In two-dimensional systems, the interface is just a line, more or less parallel to the substrate. A typical configuration may be characterized by $r(\tau)$, where τ labels the points along the
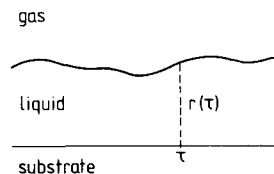

Fig. 2. An interface configuration in two (bulk) dimensions.

substrate and r is the distance above that point. (See Fig. 2.) The function $V(r)$ is an effective potential for the interface, coming from microscopic interactions between the molecules of the system and the substrate.

Being an *effective* potential, it is an implicit function of temperature (T) and can easily be "tuned" by changing T. Therefore, we may regard E as a function of T: $E(T)$. Finally, the thermal fluctuations of the interfacial position r can be translated into the quantum fluctuations[6] of a particle coordinate, so that l plays the role of *the thermal average* of the distance between the interface and the substrate. Thus, $l \to \infty$ represents an unbounded growth of the wetting film and marks the transition. In the cases we studied, $l = \infty$ for $E > 0$. Thus we label T_W as the solution to $E(T_W) = 0$. The growth of the film thickness at the transition is characterized by the exponent q. What we have shown is that, for a large variety of potentials, q is *universal* and equal to unity (Sec. III A). Such transitions are called "continuous" because l takes on all values as T_W is approached. Section III B is called "first order" because l can be both finite and infinite at T_W $(E = 0)$, depending which direction it is approached $(E < 0$ or $E > 0)$. Section III C shows the possibility of *nonuniversal behavior*, i.e., q depends on A, which can in turn depend on T since it is part of the effective potential. Readers wishing more technical details of the wetting transition may consult Ref. 7.

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