Quantum Mechanics

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WS 24/25

Sheet 3 **Saturday October 26 at 24:00**

1 A toy model of an atom

The theme of this sheet is the spectrum of Hamiltonians, and as we have seen in the lecture, the spectrum can be both continuous and discrete. In the lecture, we discuss the step potential (which has a continuous spectrum) and the infinite potential well (which has a discrete spectrum). In this exercise, we consider potentials that have both types of spectra. This makes them (slightly) more realistic models of atoms and molecules, which typically have both.[1] The calculations follow the same principles as in the lecture, although things get more involved. In particular, we will not be able to determine the discrete energy levels explicitly (like we can for the infinite potential well) but have to be satisfied with an equation that determines the eigenvalues implicitly (e.g. via numerics).

a) Recall from the lecture that the energy of a particle is given by $(H\phi)(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x)$, and the corresponding eigenvalue equation (the time-independent Schrödinger equation) is

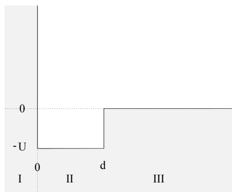
$$E\phi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x). \tag{1}$$

Now consider the special case that the potential is constant, i.e., $V(x) = V_0$. For equation (1), we make an ansatz on the form

$$\varphi(x) = Ce^{\xi x},$$

where ξ and C are *complex numbers*. Consider the two cases[2] $E > V_0$ and $E < V_0$. *For each case, determine the possible values of ξ. In particular, are they real or imaginary?* **(2 points)**

b) Piece-wise solutions for $E > 0$: Let us now turn to the specific example, namely the potential



$$V(x) = \begin{cases} +\infty & x < 0 & & \text{("Region I")} \\ -U & 0 \leq x \leq d, & U > 0, \quad d > 0 & \text{("Region II")} \\ 0 & d < x & & \text{("Region III")} \end{cases} \tag{2}$$

Here we take the first step towards showing that all energies $E > 0$ are eigenvalues to (1). From the lecture we know that in region I, where the potential is infinite, we have

$$\text{Region I:} \quad \phi_I(x) = 0 \quad \text{for} \quad x < 0,$$

but what about the the other regions? *Argue that the solutions to the time-independent Schrödinger equation* (1) *in the regions I and II take the form*

$$\text{Region II:} \quad \phi_{II}(x) = Ae^{iax} + Be^{-iax}, \quad \text{for} \quad 0 \leq x \leq d$$
$$\text{Region III:} \quad \phi_{III}(x) = Ce^{icx} + De^{-icx}, \quad \text{for} \quad d < x$$

[1] In an atom, the electrons can be bound in discrete energy levels. However, the atom can also be ionized, where the electron escapes the atom. The escaping electron could have any velocity, and thus any kinetic energy, corresponding to a continuum in the spectrum.

[2] We ignore the case $E = V_0$

and determine the constants $a > 0$ and $c > 0$ in terms of E, m, U (and $\hbar$). Here A, B, C, D are free complex parameters.

Hint: There was of course a reason for why we did a). **(4 points)**

c) Join at the interfaces: *For the case in b), apply the appropriate boundary conditions in order to show that*

$$\begin{aligned} B &= -A, \\ C &= e^{-icd}\left(i\sin(ad) + \frac{a}{c}\cos(ad)\right)A, \\ D &= e^{icd}\left(i\sin(ad) - \frac{a}{c}\cos(ad)\right)A. \end{aligned}$$

Hint: Note that the potential (3) is a combination of some aspects of the potential barrier and of the infinite potential well. Look up in the lecture notes how one treats the joining to a infinite potential 'wall', and how to treat the joining at a potential step. **(4 points)**

d) Now we are finally in position to show that each energy $E > 0$ is an eigenvalue. *For each $E > 0$ construct a wave-function ϕ_E that solves (1). More concretely, fill out the question marks below.*

$$\phi_E(x) = \begin{cases} 0 & x < 0, \\ ??? & 0 \le x \le d, \\ ??? & d < x. \end{cases} \tag{3}$$

(2 points)

e) Piece-wise solutions for $-U < E < 0$: Now we turn to the case of energies $-U < E < 0$. Again the goal is to understand the spectrum. The first step is analogous to what we did in b). *Argue that the solutions to the time-independent Schrödinger equation (1) in the regions I and II take the form*

$$\begin{aligned} &\text{Region II:} \quad \phi_{II}(x) = Ae^{iax} + Be^{-iax}, \quad \text{for} \quad 0 \le x \le d \\ &\text{Region III:} \quad \phi_{III}(x) = Ce^{-bx}, \quad \text{for} \quad d < x \end{aligned} \tag{4}$$

and determine the constants $a > 0$ and $b > 0$ in terms of E, m, U, q (and $\hbar$).

Hint: Why is there no term De^{bx} in (4)? **(4 points)**

f) Join at the interfaces: *For the case in e), show that*

$$\phi_E(x) = \begin{cases} 0 & x < 0, \\ \phi_{II}(x) & 0 \le x \le d, \\ \phi_{III}(x) & d < x \end{cases}$$

is a solution to the time-independet Schrödinger equation (1) only if

$$-\tan\left(d\sqrt{\frac{2m(U-|E|)}{\hbar^2}}\right) = \sqrt{\frac{U-|E|}{|E|}}. \tag{5}$$

Recall that E is negative, since $-U < E < 0$.

Hint: Proceed as you did in c) in order to obtain equations that relate A, B and C. Use these equations to eliminate A, B and C. **(4 points)**

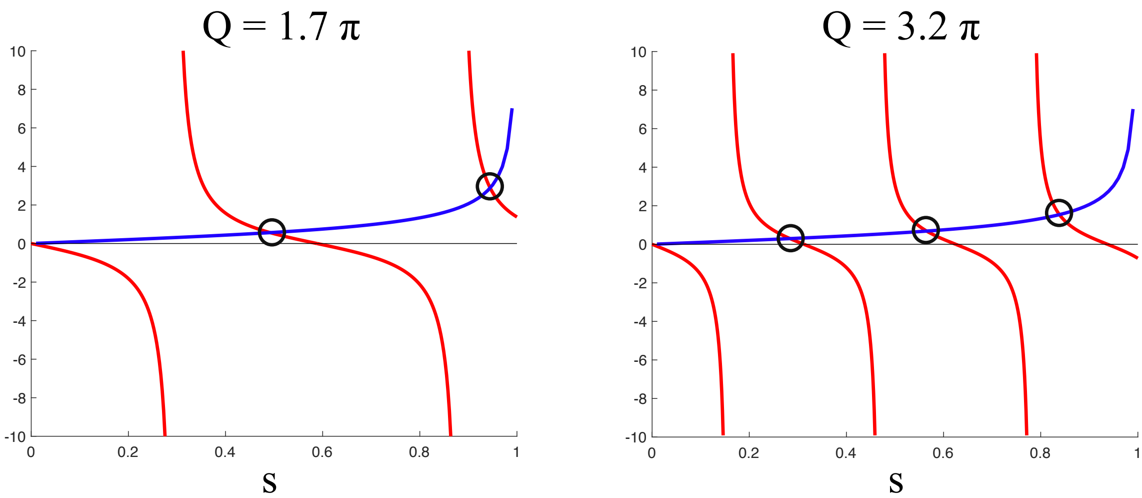
Remark: We have found that an energy E (in the interval $-U < E < 0$) only can be an eigenvalue to the time-independent Scrödinger equation if it satisfies equation (5). Unfortunately, there is no hope of solving (5) by analytical means. However, one can find the roots numerically, and one can also obtain a qualitative understanding. For both purposes it is useful to rewrite (5) in an equivalent form. With

$$s = \sqrt{1 - \frac{|E|}{U}} \tag{6}$$

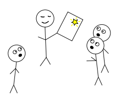
we can rewrite (5) as

$$-\tan(Qs) = \frac{s}{\sqrt{1-s^2}}, \quad Q = \sqrt{\frac{2md^2U}{\hbar^2}},$$

where $0 < s < 1$ follows since $-U < E < 0$. By this reformulation we immediately learn that the number of solutions is solely determined by the quantity Q. Moreover, the allowed energies correspond to the points where the graphs of $-\tan(Qs)$ and $\frac{s}{\sqrt{1-s^2}}$ intersect. In the figures below, the red lines correspond to $-\tan(Qs)$, while the blue lines correspond to $\frac{s}{\sqrt{1-s^2}}$. To the left is a plot for $Q = 1.7\pi$ and to the right is a plot for $Q = 3.2\pi$. Note that $-\tan(Qs)$ is a periodic function, and the larger Q is, the shorter is the period (and the more eigenvalues there are). For each root s_{root} (the circled intersections) it follows by (6) that the corresponding eigenvalue is $E = -U(1 - s^2_{\text{root}})$. Each of these discrete eigenvalues corresponds to an eigenstate where the particle is bound to the potential well (although there is the exponentially decreasing tail Ce^{-bx} sneaking out of the well). In contrast, the continuum $E > 0$ corresponds to states where the particle is 'free'; flowing in from infinity and out again.



g) Gold star exercise: This exercise gives absolutely no points! However, by solving it you do of course become the center of admiration and envy for all your peers. Moreover, your family will (obviously) bask in unbound glory for at least three generations.



What is the largest value of Q below which there is no eigenvalue E in the energy interval $-U < E < 0$?

Hint: What happens with the intersections as Q decreases? Ignore the root at $s = 0$ (which corresponds to $E = -U$). **(0 points)**

Remark: This means that for such Q, the potential is too shallow and too narrow (and the particle too light) for the well to sustain a bound state. The particle cannot get stuck there, so to speak. This is in contrast with the corresponding classical model, where the particle always can get trapped in the well if its energy is low enough.