PY 451 Notes — February 22, 2018
McIntyre Chap. 5 — One-Dimensional Potentials: Bound States

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These notes will focus on the properties of the wave functions describing bound states of one-dimensional (1-D) potentials which are functions of position *only* — $V(x)$ in 1-D. We will illustrate these properties by considering two important examples – the infinite square well and the finite square well potentials. This is opposite the order these topics are presented in the text, but I think it is more illuminating to extract these properties from a simple 1-D potential (the finite square well) and then see them in action in example after example in both 1-D and 3-D problems (like hydrogen — the H-atom). Two notes: (1) I am skipping over Section 5.1. I expect you to read this on your own; it will be especially relevant when we discuss the H-atom in detail. (2) The Dirac delta function $\delta(x - x_0)$ is used in many places below. Make sure that you know it and how to use it. If you don't, tell me at once!

A. <u>Preliminaries</u>

1.) 1-D and (> 1-D) "potential problems" use Hamiltonians with *spatially dependent and varying* potential energy functions, $V(x)$. Just as in classical mechanics, then, there are forces and changes in momentum. A nonrelativistic particle of mass m moving in a region of potential energy V which may be often be thought of as an interaction with some external source, e.g., a light electron with a heavy positively-charged nucleus, has the Hamiltonian operator — kinetic plus potential energy, $T + V$:

$$H = \frac{\hat{p}_x^2}{2m} + V(\hat{x}), \tag{1}$$

where the "hats" indicate $\hat{x}$ and $\hat{p}_x$ are operators (the abstract operators of Chapter 2) corresponding to the particle's position along the continuous (!!) one-dimensional x-axis and the x-component of its momentum. (I didn't put a hat on H because it's always understood to be an operator.) These are <u>*hermitian*</u> operators and their real eigenvalues are, respectively, position x ($-\infty < x < \infty$) and momentum p_x (often just p).

2.) For these 1-D potential problems it is often convenient and very illuminating of the physics to use the x-basis: $\{|x\rangle;\, \hat{x}|x\rangle = x|x\rangle,\ -\infty < x < \infty.\}$ Like the eigenvectors of hermitian operators we've dealt with so far, these basis vectors form a complete orthonormal set. (This can be made rigorous; just take my word for it now.)

$$\langle x|x'\rangle = \delta(x - x'); \qquad \int_{-\infty}^{\infty} dx\, |x\rangle\langle x| = \mathbf{1}. \tag{2}$$

To get a glimmer of why this is so, suppose that H in Eq. (1) has been diagonalized:

$$H|E_i\rangle = E_i|E_i\rangle \text{ with } \{|E_i\rangle; i = 1, 2, \dots\}; \tag{3}$$

$$\langle E_i|E_j\rangle = \delta_{ij}, \quad \sum_{i\geq 1} |E_i\rangle\langle E_i| = \mathbf{1}. \tag{4}$$

Define the eigenstate wave function or energy eigenfunction $\phi_{E_i}(x)$

$$\phi_{E_i}(x) = \langle x|E_i\rangle. \tag{5}$$

This wave function is *the amplitude that the particle with energy E_i is at position x* (with $-\infty < x < \infty$). Then

$$1 = \langle E_i|E_i\rangle = \int_{-\infty}^{\infty} dx \langle E_i|x\rangle\langle x|E_i\rangle = \int_{-\infty}^{\infty} dx\, \phi^*_{E_i}(x)\phi_{E_i}(x) \equiv \int_{-\infty}^{\infty} dx|\phi_{E_i}(x)|^2. \tag{6}$$

That is, $|\phi_{E_i}(x)|^2 dx$ is the *probability* that the particle with energy E_i is in the interval $(x, x+dx)$ (or in $(x - dx/2, x + dx/2)$, it doesn't matter). Thus, $\mathcal{P}_{E_i}(x) = |\phi_{E_i}(x)|^2$ is the *probability density* or "probability per unit length dx" that this particle with E_i is at position x. More generally:

$$\text{Orthonormality}: \quad \langle E_i|E_j\rangle = \delta_{ij} \implies \int_{-\infty}^{\infty} dx\, \phi^*_{E_i}(x)\phi_{E_j}(x) = \delta_{ij}; \tag{7}$$

$$\text{Completeness}: \quad \sum_{i\geq 1} |E_i\rangle\langle E_i| = \mathbf{1} \implies \sum_{i\geq 1} \phi_{E_i}(x)\phi^*_{E_i}(x') = \delta(x - x'). \tag{8}$$

That is, the set of eigenfunctions, $\{\phi_{E_i}(x);\, i \geq 1, ;\, -\infty < x < \infty\}$ is a complete orthonormal basis in the space of functions $\psi(x,t)$ that are *solutions* of the Schrödinger equation, $H|\psi(t)\rangle = i\hbar\, d|\psi(t)\rangle/dt$. More explicitly, let's expand $|\psi(t)\rangle$ in H's eigenbasis:

$$|\psi(t)\rangle = \sum_{i\geq 1} |E_i\rangle\langle E_i|\psi(t)\rangle \equiv \sum_{i\geq 1} c_i(t)|E_i\rangle = \sum_{i\geq 1} e^{-iE_i t/\hbar} c_i(0) E_i\rangle. \tag{9}$$

This implies (by "multiplying" by $\langle x|$ on both sides of the equation)

$$\psi(x,t) \equiv \langle x|\psi(t)\rangle = \sum_{i\geq 1} e^{-iE_i t/\hbar} c_i(0)\phi_{E_i}(x). \tag{10}$$

Assuming, as usual, that $\langle\psi(0)|\psi(0)\rangle = \langle\psi(t)|\psi(t)\rangle = 1$, then

$$\sum_{i\geq 1} |c_i(0)|^2 = \sum_{i\geq 1} \langle E_i|\psi(0)\rangle|^2 = \sum_{i\geq 1} \langle E_i|\psi(t)\rangle|^2 = 1. \tag{11}$$

That is, the absolute-squared amplitude, $|c_i|^2$, is the probability that the state $|\psi(t)\rangle$ is in the energy eigenstate $|E_i\rangle$. (*Note:* I am making no assumption about whether any or even all of the energies E_i are degenerate!)

3.) A note on dimensions ($[A]$ denotes the units (E for energy, L for length, T for time, of quantity A):

$$\int_{-\infty}^{\infty} \delta(x - x_0) dx = 1 \implies [\delta(x - x_0)] = L^{-1}, \tag{12}$$

$$\langle x|x'\rangle = \delta(x - x') \implies [|x\rangle] = [\langle x|] = L^{-\frac{1}{2}}, \tag{13}$$

$$\int_{-\infty}^{\infty} dx|\phi_E(x)|^2 = 1 \implies [\phi_E(x)] = L^{-\frac{1}{2}}, \tag{14}$$

$$\int_{-\infty}^{\infty} dx|\psi(x)|^2 = 1 \implies [\psi(x)] = L^{-\frac{1}{2}}. \tag{15}$$

4.) A *fundamental commutation relation* of quantum mechanics (a postulate!):

$$[\hat{x}, \hat{p}_x] = i\hbar. \tag{16}$$

More generally, in 3-D:

$$[\hat{x}_a, \hat{p}_b] = i\hbar\,\delta_{ab} \qquad (a, b = 1, 2, 3). \tag{17}$$

These commutation relations imply the famous space-momentum uncertainty relation

$$\Delta x_a \Delta p_b \geq \frac{\hbar}{2}\delta_{ab}. \tag{18}$$

This relation has an intuitively simple physical interpretation: A measurement of the x-position of a particle, i.e., localizing it to within Δx, requires imparting to it some momentum Δp_x in the x-direction. Think of observing the position of an atom using photons or other particles. Thus, measuring x disturbs p_x — and vice-versa — *at least* by an amount of order $\Delta p_x \simeq \hbar/\Delta x$. Recalling our discussion in Chapter 3 of the time dependence of the expectation value of the spin operator of a charged particle in the presence of a magnetic field, note that, if $V(x) \neq$ constant, then

$$[H, \hat{p}_x] = [V(x), \hat{p}_x] \neq 0. \tag{19}$$

In the x-representation, $\hat{p}_x$ is not diagonal:

$$\hat{p}_x \doteq -i\hbar\frac{d}{dx}. \tag{20}$$

N.B.: For any function $\psi(x)$, Eq. (20) implies

$$[\hat{x}, \hat{p}_x]\psi(x) \doteq [x(-i\hbar\frac{d}{dx}) - (-i\hbar\frac{d}{dx})x]\psi(x) = \left(i\hbar\frac{d(x)}{dx}\right)\psi(x) \equiv i\hbar\,\psi(x). \tag{21}$$

Returning to Eq. (19), let's take its expectation value in the normalized state $|\psi(t)\rangle = \exp(-iHt/\hbar)|\psi(0)\rangle$. With a slight rewrite, it becomes

$$\left\langle \psi(t)|\frac{i}{\hbar}[H, \hat{p}_x]|\psi(t)\right\rangle \equiv \left\langle \frac{i}{\hbar}[H, \hat{p}_x](t)\right\rangle_\psi = \left\langle -\frac{dV}{dx}(t)\right\rangle_\psi \equiv \left\langle \frac{d\hat{p}_x}{dt}(t)\right\rangle_\psi. \tag{22}$$

This is Ehrenfest's theorem again, true for any state $|\psi\rangle$ that is a solution of the Schrödinger equation.

B. Properties of Bound-State Wave Functions

A "bound state" is an eigenstate of the Hamiltonian which is localized in space, i.e., whose wave function does not extend to infinity and which, as a consequence of its vanishing at large distances, has an energy which is part of the discrete spectrum of energy eigenvalues of H. (Here, we are taking note that potentials, $V(x)$, which are everywhere bounded above will also have "unbound states" which correspond to energy eigenvalues greater than the maximum of V and have wave functions which do extend to infinity. These will be studied in Chapter 6.) All bound-state wave functions — not just those in 1-D — have certain properties in common. We can demonstrate these with a simple finite 1-D square well potential. In the x-representation, the Hamiltonian and its potential-energy function are

$$H = \frac{\hat{p}_x^2}{2m} + V(\hat{x}) \doteq -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \tag{23}$$

$$V(x) = \begin{cases} 0 & \text{for } |x| \leq a \\ V_0 > 0 & \text{for } |x| > a \end{cases} \tag{24}$$

The potential function with the ground and first excited state wave functions sketched:

Consider the bound-state wave function $\psi(x,t) = \langle x|\psi(t)\rangle = e^{-iEt/\hbar}\psi(x)$ corresponding to energy E.

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x). \tag{25}$$

Bound states must have energy $E < V_0$, indicated by the dashed line in the figure.

1.) The first thing to appreciate is that, since the E is a constant and V is piece-wise constant (and continuous except at single points, a set of measure zero), $\psi'(x) = d\psi(x)/dx$ must exist everywhere and so the wave function $\psi(x)$ must be *everywhere continuous.*

2.) In Region II where $V = 0$, $E = T < V_0$. Then

$$\frac{d^2\psi(x)/dx^2}{\psi(x)} = -\frac{2m}{\hbar^2}E < 0. \tag{26}$$

This is just like a simple harmonic oscillator, $\ddot{x} = -\omega^2 x$ for real ω, so that, here, $\psi(x)$ will behave sinusoidally. We see this in the ground-state $\psi_1(x)$ with about half an oscillation and in the first excited state's $\psi_2(x)$ with about one full oscillation. That this oscillation is sinusoidal is due to $V(x)$ being constant here. But the oscillatory behavior is more general: wherever $T(x) = E - V(x) < 0$ the wave function will wiggle, and the greater the kinetic energy is, the faster it wiggles. (Remember: While $\psi'(x)$ is the slope of the function ψ at x, $\psi''(x)$ is its *curvature* there! So, the greater the kinetic energy, the greater the wave function's curvature — and vice-versa. This simple fact played a very important experimental role in establishing the theoretical conjecture that quarks are "confined" by their strong interactions and, therefore, cannot be isolated — as a proton or a neutron or other bound states of quarks and antiquarks can be.)

3.) In Regions I and III, $E < V_0$, so that $T = E - V_0 < 0$. These are *classically forbidden* regions. But since ψ must be continuous at $x = \pm a$, so it must be nonzero in these regions if it was nonzero at $x = \pm|x - \epsilon|$, where ϵ is any small positive distance. An exception to this occurs if the slope $\psi'(x)$ is discontinuous at $x = a$ and/or $x = -a$ so that, e.g., $\psi(x) = 0$ at $x \geq a$ and/or $x \leq -a$. But that would require an infinite discontinuity in $V(x)$ at these points. That does happen with the infinite square well potential (and, as we shall see, with the so-called radial wave function $\psi(r)$ at $r = 0$ in 3-D potential problems — no particle can be at $r < 0$!). The points where $E - V$ changes from positive to negative are called *classical turning points* because a classical particle would turn around there and go back to a region of $T = E - V > 0$. For our finite square well in Regions I and III,

$$\frac{d^2\psi(x)/dx^2}{\psi(x)} = -\frac{2m}{\hbar^2}(E - V_0) > 0. \tag{27}$$

Like the classical equation $\ddot{x} = +\omega^2 x$ for constant real ω, Eq. (27) has the solutions

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x} \quad \text{where } \kappa = \sqrt{2m(V_0 - E)/\hbar^2} \equiv \sqrt{2mc^2(V_0 - E)}/\hbar c > 0, \tag{28}$$

where A is a constant (with dimension of $L^{-1/2}$). (The useful combination of fundamental constants $\hbar c = 0.197\,\text{GeV-fm}$, where $1\,\text{GeV} = 10^9\,\text{eV}$ and $1\,\text{fm} = 10^{-13}\,\text{cm}$, about the diameter of a proton!) Now, we must discard the solutions in which $\psi(x)$ increases exponentially at large $|x|$. Such solutions are not square-integrable, i.e., $\int_{-\infty}^{\infty} |\psi(x)|^2 dx$ is infinite and $\psi(x)$ cannot be normalized. In plain language, this is unphysical for a state bound in the potential V because its wave function is not localized to the region where $E > V$ (and $T > 0$). Thus, for the finite square well, the physically allowed solution for $|x| > a$ is[2]

$$\psi(x) = Ae^{-\kappa|x|} = \begin{cases} Ae^{-\kappa x} & \text{for } x > a \\ Ae^{\kappa x} & \text{for } x < -a \end{cases} \tag{29}$$

Again, this penetration into classically forbidden regions is a consequence of the fact that $\psi(x)$ must be continuous. Still, the exponential fall-off of $\psi(x)$ in the classically-forbidden regions comports with our physical intuition that, if we can go into such regions, it must be a for only very tiny distance, because we never see it classically. In fact, the distance we can penetrate such regions is of order $1/\kappa = \hbar/\sqrt{2m(V_0 - E)} = \hbar c/\sqrt{mc^2(V_0 - E)}$ and this is indeed very small for macroscopic masses and energies. Make estimates for yourself:

(1) For an electron of mass $m_e = 0.91 \times 10^{-27}\text{gm} = 0.511\,\text{MeV}/c^2$ in a square well potential with $V_0 = 15\,\text{eV}$ and $E = 5\,\text{eV}$. Take the half-width of the potential well to be $a = 10^{-8}$ cm and compare the penetration distance to a.

(2) For a 1 gram BB (or little ball bearing) in a cup of radius $a = 1\,\text{cm}$ and height $h = 2\,\text{cm}$. The cup is on a table at the surface of the earth and the BB has kinetic energy of $T = 1000\,\text{erg}$. The BB is subject to the earth's gravitational potential energy, $V(x) = mgx$, where $x = 0$ is the inside bottom of the cup. Make the same comparison as in (1) and compare the two values of κ and κa that you get.

For more general potentials than the simple piece-wise continuous square well, the fall-off in classically forbidden regions is still exponential but not with the first power of x. We'll see

[2] That the coefficient A of the exponential in Eq. (29) is the same for $x > a$ and $x < -a$ is consequence of $V(x) = V(-x)$. We shall understand this when we discuss invariance under space reflection or *parity*, below.

that when we consider the harmonic oscillator whose potential is $V(x) = \frac{1}{2}m\omega^2 x^2$. Do you think the fall-off beyond $|x_{\rm cl.}| = \sqrt{2E/m\omega^2}$ is faster than it is in the finite square well or slower? Why?

4.) Back in Region II, there are three more things of importance to note: First, the matter of <u>nodes</u> of the wave function: The ground-state wave function $\psi_1(x)$ vanishes only at infinity. It has no zeroes, or "nodes" at finite x. The first excited state wave function $\psi_2(x)$ has one node — at $x = 0$. If I had drawn the second excited state, $\psi_3(x)$, it would have two nodes — one at $0 < x_3 < a$, the other at $-a < -x_3 < 0$. This is a property of <u>*all*</u> bound-state wave functions in any number of dimensions: the wave function of each successive (discrete) energy level has one more node than the next lower level. Furthermore, all these nodes must occur in the classically-allowed region, the one in which $E > V(x)$. That is because once we are in a region of x for which $E < V(x)$, the curvature $(d^2\psi(x)/dx^2)/\psi(x) = 2m(V(x) - E)/\hbar^2 > 0$, i.e., it is concave up if $\psi(x) > 0$ and concave down if $\psi(x) < 0$. Since the wave function must be decreasing exponentially there (with some positive power of x), it <u>*cannot*</u> cross the x-axis and change sign so that the curvature changes sign; if it does, the wave function will blow up at large $|x|$! This increased wiggling of ψ with increasing energy E in the classically-allowed region simply means that the particle has increasing kinetic energy, $T(x) = E - V(x)$.

5.) It is easy to understand why the energy levels of bound states are quantized. The Schrödinger is a wave equation, not unlike the harmonic oscillator equation for an oscillating string. The boundary conditions that $\psi(x)$ vanish at $x = \pm\infty$ are like those for a string with both ends fixed and, as you know, such a string can only support certain frequencies, $\nu_n = nv/2L$ where L is the length of the string and v is the characteristic velocity of a traveling wave on the string. It's as simple as that!

6.) Consider the Schrödinger equation in 1-D for the bound-state wave functions:

$$H\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x). \tag{30}$$

If $V(x) = V(-x)$, as it is for the finite square well in Eq.(23), then H is invariant under *space reflection*, $x \to -x$. Reversing the sign of x in Eq.(30) implies that, if $\psi(x)$ is a solution, so is $\psi(-x)$. This further implies that the *even* and *odd* wave functions,

$$\psi_\pm(x) = \frac{1}{\sqrt{2}}\left(\psi(x) \pm \psi(-x)\right) \tag{31}$$

are solutions with the *same* energy E. But $\psi_-(x)$ has one more node than $\psi_+(x)$; it's at $x = 0$. So ψ_+ and ψ_- cannot have the same energy and, so, both cannot be nonzero. As the drawing on page 4 indicates, the wave functions with energies $E_1, E_3, E_5, \dots$ have $n_+ = 0, 2, 4, \dots$ nodes while those with energies $E_2, E_4, E_6, \dots$ have $n_- = 1, 3, 5, \dots$ nodes with the energy ordering $E_1 < E_2 < E_3 < E_4 < \cdots$. This symmetry under space inversion is called <u>*parity invariance*</u>. Note that, for the parity-invariant $V(x) = V(-x)$ in 1-D, there is no degeneracy implied by parity. There is a parity operator $\boldsymbol{P}$ that changes the sign of x (and for which $\boldsymbol{P}^2 = 1$) and it commutes with the Hamiltonian, $[H, \boldsymbol{P}] = 0$, but there is no degeneracy associated with it. This non-degeneracy of the energy eigenvalues $E_1, E_2, E_3, \dots$ is a special feature of 1-D; it is not necessarily true in 3-D. (See the H-atom, e.g.)

7.) Finally, if $E > V_0$, (more generally, $E > V(x)$ everywhere), $\psi(x)$ oscillates everywhere and it wiggles faster for larger $T = E - V(x)$ and more slowly for smaller kinetic energy. Such a wave function is *apparently not* normalizable! But it is certainly physical, because there is no reason (classically or quantum mechanically) that a particle can't have $E > V$ everywhere if V is bounded from above. This is the subject of Chapter 6.