Section 11 - Wave Mechanics

"[J]e tâchais de découvrir, dans les bruits … des flots, des mots que les autres hommes n'entendaient point, et j'ouvrais l'oreille pour écouter la révélation de leur harmonie…"

Gustave Flaubert, Novembre

In the last several sections, we discussed how a particle can be, to some extent, represented by a wave. In the old quantum mechanics, this conceptual link was not a strong one; the De Broglie wave was referred to as the *pilot wave*, a wave that somehow accompanies the particle and guides its motion. In this section, we'll discuss the *Schrödinger picture*, where the particle is completely described as a wave. To be sure, there were a number of other pictures developed in the 20^{th} century, such as the *Heisenberg picture*, which was eventually shown to be the same as the Schrödinger picture in matrix form.

Operators

Before we start, let's talk a little about *operators*. You may be familiar with operators from linear algebra, but if not, an operator is just an instruction as to what to do with a function. For example, the differentiation operator D_x tells us to take the derivative of a function with respect to x:

$$\widehat{D}_x = \frac{d}{dx}, \qquad \text{so } \widehat{D}_x F = \frac{dF}{dx}.$$

Operators are often distinguished by the addition of a caret over the symbol. In linear algebra, operators are represented by matrices and operate on vectors. As a simple example, here is an operator that will rotate a vector **A** in the x-y plane by π:

$$\widehat{R}_\pi \vec{A} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} A_x \\ A_y \end{bmatrix} = \begin{bmatrix} -A_x \\ -A_y \end{bmatrix} = -\begin{bmatrix} A_x \\ A_y \end{bmatrix} = -\vec{A}.$$

Let's look at another example. Let's rotate **A** CCW by π/2:

$$\widehat{R}_{\frac{\pi}{2}} \vec{A} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} A_x \\ A_y \end{bmatrix} = \begin{bmatrix} -A_y \\ A_x \end{bmatrix}.$$

There's an important difference between these two examples. In the first, the resulting vector is a multiple of the original vector, in this case by -1. In the second case, there is no number (well, certainly no real number) that will multiply the result to give back **A**. In such a lucky situation as the first, the vector is said to be an *eigenvector* of the operator, and the multiple factor is an *eigenvalue* of the operator:

$$\widehat{\Lambda} \vec{V} = \lambda \vec{V}.$$

In our discussion, we'll be using functions instead of vectors, but the idea is the same. For example,

$$\widehat{D}_x\, e^{\lambda x} = \lambda\, e^{\lambda x}\,.$$

So, the exponential function is an *eigenfunction* of the differential operator, with eigenvalue λ.

The Schrödinger Picture

It is said that one cannot derive the Schrödinger wave equation, but certainly we can make a guess based on certain requirements.

1) The particle is represented by a wave function $\Psi(\mathbf{r}, t)$. The function is continuous and single-valued. Its spatial derivative is also continuous, except if the potential energy goes to infinity. See NOTE ONE.
2) The wave equation should be analogous to the classical mechanical wave equation:
$$\frac{\partial^2 Y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 Y}{\partial t^2} \quad \text{(written here for } 1-\text{d).}$$
3) The picture should be consistent with the De Broglie notion, which demonstrated some success in the old quantum mechanics. That is, the particle's representation as a wave should have wavelength $\lambda = p/h$ and energy $E = hf = \omega\hbar$.
4) We interpret the square[1] of the wave $\Psi^2(\mathbf{r}, t)$ as representing the probability that the particle is in a given position. This should make sense in analogy with light waves, in that the light intensity is related to the square of the electric field, and represents the probability of a given photon landing in a particular spot, for example, on a screen. The function $\Psi^2(\mathbf{r}, t)$ is called the *probability density*. We require that
$$\int \Psi^2(\mathbf{r}, t)\, dV = 1\,,$$
that is, the particle must be somewhere.
5) We require linear solutions. That is, if Ψ_1 and Ψ_2 are solutions, then $a\Psi_1 + b\Psi_2$ is also a solution.
6) The model should be consistent with classical energy considerations: $E_{TOTAL} = K + U$.
7) If the potential energy is constant, i.e., there are no forces, then momentum and energy are conserved.

O.K. Let's consider your basic one dimensional wave of frequency f and wavelength λ. Remember that the wave vector $k = 2\pi/\lambda$ and $\omega = 2\pi f$. Also remember that the momentum $p = h/\lambda = \hbar k$ and $E = \omega\hbar$. We're going to use a complex representation[2] of the wave:

$$\Psi(x, t) = Ae^{i(kx - \omega t + \varphi)},$$

where phi is the phase angle, which we'll ignore from here on. Let's differentiate with respect to x:

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[1] This is the Born interpretation. We'll be more careful about this later.
[2] $e^{ix} = \cos(x) + i\sin(x)$.

$$\frac{\partial \Psi}{\partial x} = \ ik\, Ae^{i(kx-\,\omega t)} = ik\,\Psi.$$

Keeping in mind from our discussion of waves in PHYS I that k = 2π/λ, this looks promising! Let's construct an operator that will return the particle's momentum; try

$$\hat{p}_x = \ -i\hbar\frac{\partial}{\partial x},$$

so that

$$\hat{p}_x\Psi = \ -i\hbar\frac{\partial \Psi}{\partial x} = -i\hbar(ik\,\Psi) = \ k\hbar\,\Psi = \frac{2\pi}{\lambda}\frac{h}{2\pi}\ \Psi = \frac{h}{\lambda}\ \Psi = p\Psi\,.$$

So, now what about the particle's kinetic energy? We might remember that $K = p^2/2m$, so let's try

$$\hat{K} = \ \frac{1}{2m}\ \hat{p}_x^2 = \ \frac{1}{2m}\hat{p}_x\hat{p}_x = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) = \frac{-\,\hbar^2}{2m}\ \frac{\partial^2}{\partial x^2},$$

$$\hat{K}\Psi = \frac{-\,\hbar^2}{2m}\ \frac{\partial^2 \Psi}{\partial x^2} = \frac{-\,\hbar^2}{2m}(ik)^2\Psi = \ \frac{\hbar^2 k^2}{2m}\Psi\ = \ \frac{p^2}{2m}\Psi = \ K\,\Psi\,.$$

Let's try for the total energy, E, which is most directly related to ω, so we'll take a time derivative this time:

$$\frac{\partial \Psi}{\partial t} = \ -i\omega\ \ Ae^{i(kx\ \ \ \omega t+\phi)} = \ -i\omega\Psi,$$

so let

$$\hat{E} = i\hbar\frac{\partial}{\partial t}.$$

Then,

$$\hat{E}\,\Psi = i\hbar\frac{\partial \Psi}{\partial t} = i\hbar(-i\omega)\ \Psi = \ \hbar\omega\Psi = E\,\Psi.$$

There are, of course, some problems with this, most of which we can clean up. First, we assumed a wave of infinite extent with well-defined values λ and ω (and therefor, for momentum and energy), even though any value of p and E would be allowed. That's not particularly useful. If we want our particle to be localized and not spread out over the entire universe, we need to allow more values of momentum, or, if you prefer, have more uncertainty in the momentum, per the Heisenberg uncertainty principle. See NOTE TWO for a discussion in more detail. This is still O.K., *per* requirement 5 above; solutions with different momentum values are still collectively a solution.

Lastly, let's look at the potential energy, U(x). The wave function doesn't contain any quantities related to U. What can we do to the wave function to end up with the potential energy multiplied by the wave function?

The operator is the potential energy function itself!

$$\widehat{\mathrm{U}} = \mathrm{U(x)} \quad \rightarrow \quad \widehat{\mathrm{U}}\,\Psi = \mathrm{U(x)}\Psi\,.$$

So, let's put it all together:

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2\Psi}{\partial \mathrm{x}^2} + \mathrm{U(x)}\Psi = \mathrm{i}\hbar\frac{\partial\Psi}{\partial \mathrm{t}} \quad \rightarrow \quad \mathrm{K}\Psi + \mathrm{U}\Psi = \mathrm{E}\Psi \quad \rightarrow \quad \mathrm{K} + \mathrm{U} = \mathrm{E}.$$

And, here we have arrived at the one dimensional, time dependent Schrödinger equation. We're not going to do any problems like that, so let's simplify things a bit. If the wave function does not evolve with time, then we're talking about a *stationary state*, analogous to a standing wave in mechanical wave mechanics. In such cases, the function acquires an envelope $\psi(x)$ within which it oscillates as $e^{\pm i\omega t}$ and we can separate out the temporal behavior of the function from the spatial behaviour:[3]

$$\Psi(\mathrm{x,t}) = \psi(\mathrm{x})\,\mathrm{T(t)} = \psi(\mathrm{x})\,\mathrm{e}^{\pm\mathrm{i}\omega\mathrm{t}}\,.$$

The kinetic and potential energy operators will have no effect on the time dependent term T, and the total energy operator will simply return E from T(t).

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2(\psi\mathrm{T})}{\partial \mathrm{x}^2} + \mathrm{U(x)}(\psi\mathrm{T}) = \mathrm{i}\hbar\frac{\partial(\psi\mathrm{T})}{\partial \mathrm{t}} \quad \rightarrow \quad \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2\psi}{\partial \mathrm{x}^2}\mathrm{T} + \mathrm{U(x)}\psi\,\mathrm{T} = \mathrm{i}\hbar\,\psi\frac{\partial\mathrm{T}}{\partial \mathrm{t}} = \mathrm{E}\,\psi\,\mathrm{T}\,.$$

Dividing through by T, we arrive at the one dimensional time-independent equation,

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{d^2\psi}{d\mathrm{x}^2} + \mathrm{U(x)}\psi = \mathrm{E}\psi\,.$$

See NOTE THREE for the extension to three dimensions.

Just FYI, the sum of the kinetic and potential energy operators is sometimes written as H:

$$\widehat{\mathrm{H}}\psi = \mathrm{E}\psi\,.$$

[3] Ψ is used to represent the function with both spatial and temporal dependences; ψ represents the spatial only function.

Particle in a Box

Once again, let's examine the square well, a one dimensional box from x = 0 to x = L, with impenetrable walls at each end. The potential energy function is then

Region I: $x < 0$ $U_I = \infty$

Region II: $0 < x < L$ $U_{II} = 0$

Region III: $x > L$ $U_{III} = \infty$

In Regions I and III, the solution for ψ is clearly zero. For Region II, the Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi\,.$$

So, our solution is a function that is proportional to the <u>negative</u> of its own second derivative; there are two possibilities:

$$\psi(x) = A\sin(ax) + B\cos(bx).$$

Since the function must be continuous, it must equal zero at x = 0 and x = L to match the solutions in Regions I and III. That eliminates the cosine and puts limits on the allowed values for a in the sine function:

$$aL = n\pi \quad n = 1, 2, 3, 4, \ldots \quad \rightarrow \quad a = \frac{n\pi}{L}$$

So,

$$\psi_n(x) = A_n \sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, 4, \ldots\,.$$

Substitute this into the Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{d^2\left(A_n \sin\left(\frac{n\pi}{L}x\right)\right)}{dx^2} = E_n A_n \sin\left(\frac{n\pi}{L}x\right)$$

$$\frac{-\hbar^2}{2m}\left(\frac{n\pi}{aL}\right)^2\left(-A_n \sin\left(\frac{n\pi}{L}x\right)\right) = E_n A_n \sin\left(\frac{n\pi}{L}x\right)$$

$$\frac{\hbar^2}{2m}\left(\frac{n\pi}{aL}\right)^2 = E_n$$

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} = n^2 \frac{h^2}{8mL^2},$$

as before when we made use of the Wilson-Sommerfeld relationship.

Next, we need to take care of requirement four from above. This process is called *normalization*. We will find the values of A_n so that the probability of finding the particle somewhere is 100%.

$$\int_{-\infty}^{+\infty} \psi^2 \, dx = 1$$

$$\int_{-\infty}^{+\infty} \psi^2 \, dx = \int_0^L \psi^2 \, dx = \int_0^L A_n^2 \sin^2\left(\frac{n\pi}{L}x\right) dx = A_n^2 \left[\frac{x}{2} - \frac{\sin\left(\frac{2n\pi x}{L}\right)}{\frac{4n\pi}{L}}\right]_0^L$$

$$= \frac{A_n^2}{2} L \quad \text{for all n.}$$

This leaves us with

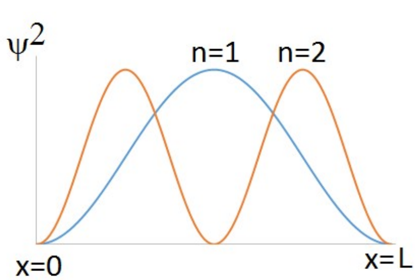
$$A_n = \sqrt{\frac{2}{L}},$$

independent of n. Finally, for Region II the wave functions and their corresponding energy eigenvalues are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad E_n = n^2 \frac{h^2}{8mL^2}.$$

The probability densities between x = 0 and x = L are then

$$\psi_n^2 = \frac{2}{L} \sin^2\left(\frac{n\pi}{L}x\right).$$



The figure shows sketches of the first two probability densities (not the wave functions). We can see that the probability of finding our particle in any given spot in the box is NOT constant as one might expect classically, which is that occupancy of every interval of length *d*x should be equally probable (see NOTE FOUR). What's more, the distribution of the probability density changes from one state to another. Let's try some calculations. What is the probability that a particle in the n = 1 state is located between x = 0 and x = L/4? Classically, the result should of course be 25%. However, we see that

$$P\left(0 < x < \frac{L}{4}; n = 1\right)$$

$$= \int_0^{L/4} \psi_1^2\, dx$$

$$= \int_0^{L/4} \frac{2}{L}\sin^2\left(\frac{\pi}{L}x\right) dx = \frac{2}{L}\left[\frac{x}{2} - \frac{\sin\left(\frac{2\pi x}{L}\right)}{\frac{4\pi}{L}}\right]_0^{L/4} = 0.091 = 9.1\ \%.$$

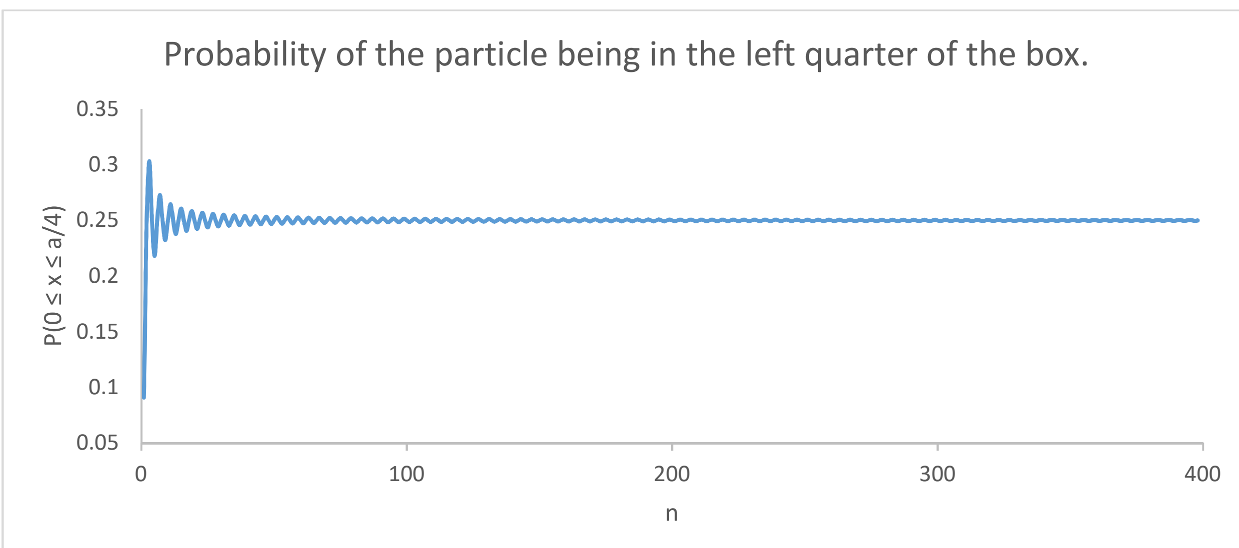
However, for the n = 2 function, we can see from the sketch and without any calculation, that the probability is 25% (See NOTE FOUR). For fun, let's do the calculation for n = 3:

$$P\left(0 < x < \frac{L}{4}; n = 3\right)$$

$$= \int_0^{L/4} \psi_3^2\, dx$$

$$= \int_0^{L/4} \frac{2}{L}\sin^2\left(\frac{3\pi}{L}x\right) dx = \frac{2}{L}\left[\frac{x}{2} - \frac{\sin\left(\frac{6\pi x}{L}\right)}{\frac{12\pi}{L}}\right]_0^{L/4} = 0.30 = 30\%.$$

One last comment: we should expect, *per* the correspondence principle, that the quantum solution should become equivalent to the classical solution as n increases. The figure below shows the probability of the particle being in the left quarter of the box for different values of energy level, n. We can see that the probability trends towards 25%.



HOMEWORK 11-1

Calculate the probability that a particle in the n = 2 state is in the left third of the box.

Simple Harmonic Oscillator

Next, we will return to the simple harmonic oscillator. The force acting on the particle is, as for a mass on a spring,

$$F(x) = -Cx,$$

$$U(x) = \tfrac{1}{2}Cx^2 ,$$

$$\text{with } \omega_o = \sqrt{\frac{C}{m}}$$

being the frequency of oscillation of a classical system with the same parameters. Since we've been using k as the wave vector in this section, we'll use C for the spring constant to avoid confusion.

The one dimensional time independent Schrödinger equation for the SHO is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}Cx^2\,\psi = E\psi .$$

This may look fairly simple, but the solution involves solving this differential equation, then an ancillary differential equation. We're going to take a different path. We'll generate an *Ansatz Erlösung*, which is just a fancy German way of saying 'a guess.' We should probably expect a superficial similarity with the solution for the infinite well, in the sense that the wave function should be symmetric for the lowest energy, and should tail off to zero in each direction but without the abrupt termination like we had at the infinitely hard wall. Let's try

$$\psi_0(x) = A_0 e^{-\alpha x^2}.$$

Then,

$$\frac{d\psi_0}{dx} = -2A_0\alpha x e^{-\alpha x^2} \text{ and } \frac{d^2\psi_0}{dx^2} = 4A_0\alpha^2 x^2 e^{-\alpha x^2} - 2A_0\alpha e^{-\alpha x^2} = (4\alpha^2x^2 - 2\alpha)A_0 e^{-\alpha x^2}$$
$$= (4\alpha^2x^2 - 2\alpha)\,\psi_0 .$$

Substituting,

$$\frac{-\hbar^2}{2m}(4\alpha^2x^2 - 2\alpha)\,\psi_0 + \tfrac{1}{2}C\,x^2\,\psi_0 = E_0\,\psi_0$$

$$-\frac{2\alpha^2\hbar^2}{m}x^2 + \frac{\alpha\hbar^2}{m} + \tfrac{1}{2}C\,x^2 = E_0 .$$

Collecting like powers[4] gives us two equations:

$$-\frac{2\alpha^2\hbar^2}{m}+\frac{1}{2}C = 0. \quad \rightarrow \quad \alpha = \sqrt{\frac{Cm}{4\hbar^2}}$$

$$\frac{\alpha\hbar^2}{m} = E_0 \quad \rightarrow \quad E_0 = \frac{\alpha\hbar^2}{m} = \sqrt{\frac{Cm}{4\hbar^2}}\frac{\hbar^2}{m} = \frac{1}{2}\sqrt{\frac{C}{m}}\hbar = \frac{1}{2}\omega_o\hbar.$$

So, our guess is indeed a solution to the Schrödinger equation. Note however that this result for the energy does not agree with the old quantum mechanics, where the lowest energy level allowed was $\hbar\omega_o$. Hold on to this for a while.

We also need to normalize ψ_0:

$$\text{Require} \int_{-\infty}^{+\infty} A_0^2 e^{-2\alpha x^2}\, dx = 1.$$

$$A_0^2 \int_{-\infty}^{+\infty} e^{-2\alpha x^2}\, dx = A_0^2\sqrt{\frac{\pi}{2\alpha}} = A_0^2\sqrt{\frac{\pi}{2\sqrt{\frac{Cm}{4\hbar^2}}}} = A_0^2\sqrt{\frac{\pi\hbar}{\sqrt{Cm}}} = 1.$$

$$A_0 = \left(\frac{Cm}{\pi^2\hbar^2}\right)^{1/8}.$$

Then, finally,

$$\psi_0 = \left(\frac{Cm}{\pi^2\hbar^2}\right)^{1/8} e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2}.$$

Not too bad, but finding the next wave function and energy looks difficult. Well, we could guess again; by analogy with the particle in a box, the wave function should be odd with a zero at x = 0, so we could try

$$\psi_1(x) = A_1 x e^{-\beta x^2}.$$

HOMEWORK 11-2

Verify that the function $\psi_1(x)$ above is indeed a solution to the harmonic oscillator problem. Find the corresponding energy of the system, E_1.

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[4] We can do this because, at one point, x = 0. Then, $\frac{\alpha\hbar^2}{m} = E_0$. But since these are constant terms, this is always true. Subtracting these terms from the original equation and dividing what's left by x^2 tells us that $-\frac{2\alpha^2\hbar^2}{m}+\frac{1}{2}C = 0$.

As we'll see later, this is actually the correct form. But we don't want to be guessing the eigenfunction for every possible value of n, and it would turn out to be very difficult after n = 1, anyway.[5] We'd like a method that will give us the actual functions.

OUTSIDE THE COMFORT ZONE 11-1*

Turns out, there is an alternate, 'outside of the box,' solution method.[6] It's a bit tedious, but very systematic, and it will give us the eigenfunctions and energy levels. The operators introduced below go by several names, but we'll call them the *ladder operators*. We won't worry about where they come from,[7] but we will test them to see if they do what we want them to do (see NOTE FIVE). For reasons that will become clear, SU is the *step up operator* and SD is the *step down operator*:[8]

$$\widehat{SU} = -i\sqrt{\frac{\hbar}{2m\omega_o}}\frac{\partial}{\partial x} + i\sqrt{\frac{m\omega_o}{2\hbar}}x \quad \rightarrow \quad \widehat{SU} = B_1\frac{\partial}{\partial x} + B_2 x$$

$$\widehat{SD} = -i\sqrt{\frac{\hbar}{2m\omega_o}}\frac{\partial}{\partial x} - i\sqrt{\frac{m\omega_o}{2\hbar}}x \quad \rightarrow \quad \widehat{SD} = B_1\frac{\partial}{\partial x} - B_2 x\,.$$

We have some math to do, so the B's will make that a bit easier.

So, consider the following

$$\tfrac{1}{2}\hbar\omega_o\left(\widehat{SD}\,\widehat{SU} + \widehat{SU}\,\widehat{SD}\right)\psi = E\,\psi;$$

We'll show that this is the same as the Schrödinger equation for the SHO. Let's do one term at a time:

$$\begin{aligned}\widehat{SD}\,\widehat{SU}\,\psi = &\left(B_1\frac{\partial}{\partial x} - B_2 x\right)\left(B_1\frac{\partial}{\partial x} + B_2 x\right)\psi\\ &= B_1^2\,\frac{\partial^2\psi}{\partial x^2} + B_1B_2\psi + B_1B_2x\frac{\partial\psi}{\partial x} - B_1B_2x\frac{\partial\psi}{\partial x} - B_2^2x^2\psi\\ &= B_1^2\,\frac{\partial^2\psi}{\partial x^2} + B_1B_2\psi + -B_2^2x^2\psi\end{aligned}$$

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[5] For example, $\psi_2 = A(1\text{-}Bx^2)\exp(-Cx^2)$ and $\psi_3 = A(x - Bx^3)\exp(-Cx^2)$. Not particularly obvious.
[6] Ziman reference.
[7] Actually, it's not all that hard, and involve some factoring of the operators.
[8] These are usually called the *raising operator* and the *lowering operator*, but I want to avoid some possible confusion later in the course.

and

$$\widehat{SU}\,\widehat{SD}\,\psi = \left(B_1\frac{\partial}{\partial x} + B_2 x\right)\left(B_1\frac{\partial}{\partial x} - B_2 x\right)\psi$$

$$= B_1^2\,\frac{\partial^2\psi}{\partial x^2} - B_1 B^2\psi - B_1 B_2 x\frac{\partial\psi}{\partial x} + B_1 B_2 x\frac{\partial\psi}{\partial x} - B_2^2 x^2\psi$$

$$= B_1^2\,\frac{\partial^2\psi}{\partial x^2} - B_1 B_2\psi - B_2^2 x^2\psi\,.$$

Putting them back together,

$$\left(\widehat{SD}\,\widehat{SU} + \widehat{SU}\,\widehat{SD}\right)\psi = 2B_1^2\,\frac{\partial^2\psi}{\partial x^2} - 2B_2^2 x^2\psi$$

$$\tfrac{1}{2}\,\hbar\omega_o\left(\widehat{SD}\,\widehat{SU} + \widehat{SU}\,\widehat{SD}\right)\psi = \tfrac{1}{2}\,\hbar\omega_o\left(\frac{-2\hbar}{2m\omega_o}\,\frac{\partial^2\psi}{\partial x^2} - \frac{-2m\omega_o}{2\hbar}x^2\psi\right) = E\psi$$

$$\left(\frac{-\hbar^2}{2m}\,\frac{\partial^2\psi}{\partial x^2} + \frac{m\omega_o^2}{2}x^2\psi\right) = E\psi$$

$$\frac{-\hbar^2}{2m}\,\frac{\partial^2\psi}{\partial x^2} + \tfrac{1}{2}\,C\,x^2\psi = E\psi\,.$$

O.K., so our proposed combination of ladder operators is the same as the left hand side of the Schrödinger equation for the one dimensional SHO. Let's see if we can make use of this.

Let's suppose that each of SU and SD have a family of functions[9] ξ_0, ξ_1, ξ_2, …, ξ_n, … such that

$$\widehat{SD}\,\xi_n = n^{1/2}\xi_{n-1} \text{ and } \widehat{SU}\,\xi_n = (n+1)^{1/2}\xi_{n+1}\,.$$

<u>If</u> said functions exist, would they solve the Schrödinger equation? Let's test them:

$$\tfrac{1}{2}\,\hbar\omega_o\left(\widehat{SD}\,\widehat{SU} + \widehat{SU}\widehat{SD}\right)\xi_n = E\,\xi_n$$

$$\tfrac{1}{2}\,\hbar\omega_o\left(\widehat{SD}\left(\widehat{SU}\xi_n\right) + \widehat{SU}\left(\widehat{SD}\xi_n\right)\right) = E\,\xi_n$$

$$\tfrac{1}{2}\,\hbar\omega_o\left(\widehat{SD}\left((n+1)^{1/2}\xi_{n+1}\right) + \widehat{SU}\left(n^{1/2}\xi_{n-1}\right)\right) = E\,\xi_n$$

$$\tfrac{1}{2}\,\hbar\omega_o\left((n+1)^{1/2}\widehat{SD}\xi_{n+1} + n^{1/2}\widehat{SU}\xi_{n-1}\right) = E\,\xi_n$$

Now, careful on this step:

[9] Not eigenfunctions, though.

$$\frac{1}{2}\hbar\omega_o\left((n+1)^{1/2}(n+1)^{1/2}\xi_n + n^{1/2}n^{1/2}\xi_n\right) = E\,\xi_n$$

$$\left(n+\frac{1}{2}\right)\hbar\omega_o\ \xi_n = E\,\xi_n \quad n = 0, 1, 2, 3, \ldots.$$

It appears that our ξ_n functions are indeed the solutions ψ_n to the SHO equation, <u>if</u> their corresponding energy levels are given by

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega_o, \quad n = 0, 1, 2, 3, \ldots.$$

Note that the Wilson-Sommerfeld approach actually wasn't so bad, in that the energy levels actually <u>are</u> evenly spaced by $\hbar\omega_o$; just the value of the starting point was off.

Our last task is to find the actual wave functions. Again, tedious but straightforward if we know even just one of them. Luckily, we already have $\xi_o = \psi_o$:

$$\psi_0 = \left(\frac{Cm}{\pi^2\hbar^2}\right)^{1/8} e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2}.$$

Then, we don't have to solve the Schrödinger equation to find the rest of the solutions, we'll just use the step up operator to find them. For example, to find ψ_1:

$$\widehat{SU}\psi_0 = (0+1)^{1/2}\psi_1 = \psi_1,$$

$$\begin{aligned}
\psi_1 = \widehat{SU}\psi_0 &= \left(B_1\frac{\partial}{\partial x} + B_2 x\right)\psi_0 = \left(B_1\frac{\partial}{\partial x} + B_2 x\right)\left(\frac{Cm}{\pi^2\hbar^2}\right)^{1/8} e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2} \\
&= \left(\frac{Cm}{\pi^2\hbar^2}\right)^{1/8}\left(B_1\frac{\partial}{\partial x}e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2} + B_2 x\, e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2}\right) \\
&= \left(\frac{4}{\pi}\left(\frac{Cm}{\hbar^2}\right)^{3/2}\right)^{1/4} x\, e^{-\sqrt{\frac{Cm}{4\hbar^2}}x^2}.
\end{aligned}$$

You might want to double check the last step of this calculation, which I omitted. Is this solution consistent with the result from HOMEWORK 11-2?

The rest of the eigenfunctions, ψ_n, can be found in the same manner:[10]

[10] Different step up and step down operators can be used for other systems, although in some cases, direct solution of the Schrödinger equation may be easier. For the SHO, they are worth the effort.

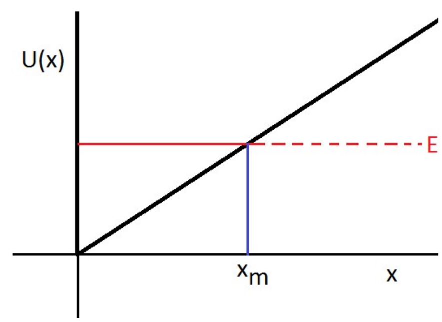
$$\widehat{SU}\psi_1 = (1+1)^{1/2}\psi_2 \quad \rightarrow \quad \psi_2 = \frac{\widehat{SU}\psi_1}{\sqrt{2}} \ ,$$

$$\widehat{SU}\psi_2 = (2+1)^{1/2}\psi_3 \quad \rightarrow \quad \psi_3 = \frac{\widehat{SU}\psi_2}{\sqrt{3}} \ ,$$

$$\widehat{SU}\psi_3 = (3+1)^{1/2}\psi_4 \quad \rightarrow \quad \psi_4 = \frac{\widehat{SU}\psi_3}{2} \ , \ et\ c.$$

Bouncing Particle

Several sections ago, we used the quantization of the action to examine the case of a particle subject to a constant force F for x > 0 and an impenetrable barrier at the origin. Our goal now is to find the exact allowed energy levels of a particle trapped in this potential well, U(x) = Fx. As before, the maximum position x_m in the +x direction depends on the particle's energy. The right hand turning point is found by setting K = 0 and so E = F x_m, and so x_m = E/F.



For x>0, the Schrödinger equation is then

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathrm{Fx}\,\psi = \mathrm{E}\psi$$

We're going to use a change of variable, so in preparation, we'll subtract Eψ from both sides and multiply by $-(2m/\hbar^2F^2)^{1/3}$ to obtain

$$\left(\frac{\hbar^2}{2mF}\right)^{2/3}\frac{d^2\psi}{dx^2} - \left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(x - \frac{E}{F}\right)\psi = 0$$

and let

$$w = \left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(x - \frac{E}{F}\right) .$$

Note that w is a dimensionless quantity and that w = 0 when x = x_m, the classical turning point on the right. Continuing,

$$\frac{dw}{dx} = \left(\frac{2mF}{\hbar^2}\right)^{1/3} \quad \text{and} \quad \frac{d^2w}{dx^2} = 0.$$

Making use of the chain rule[11] for the derivative results in,

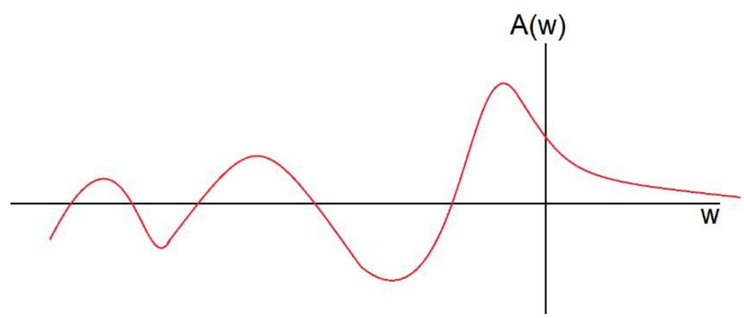
$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dw^2}\left(\frac{dw}{dx}\right)^2 = \frac{d^2\psi}{dw^2}\left(\left(\frac{2mF}{\hbar^2}\right)^{1/3}\right)^2 = \frac{d^2\psi}{dw^2}\left(\frac{2mF}{\hbar^2}\right)^{2/3}$$

and substitution results in

$$\left(\frac{\hbar^2}{2mF}\right)^{2/3}\left(\frac{d^2\psi}{dw^2}\left(\frac{2mF}{\hbar^2}\right)^{2/3}\right) - \left(\frac{2mF}{\hbar^2}\right)^{\frac{1}{3}}\left(x - \frac{E}{F}\right)\psi = 0\,,$$

$$\frac{d^2\psi}{dw^2} - w\,\psi = 0.$$

The solutions to this differential equation are well known[12], the *Airy functions* A(w) and B(w). B(w) grows to infinity as w goes to infinity, so we can't use it as our solution, because our wave functions must be able to be normalized. On the other hand, A(w) falls off to zero as w increases, as we would expect for an object attempting to penetrate into a barrier. Here is a rough sketch of A(w).



Notice that there are values of w for which A(w) = 0. These values of w are, appropriately enough, called the *zeros of A(w)*, Z_n, and their values are also well-known. The first ten values (there is an infinite number of zeros), counting from w = 0 toward negative infinity, are listed in the table at right.

n	Z_n
1	-2.33810
2	-4.08794
3	-5.52055
4	-6.78670
5	-7.94413
6	-9.02265
7	-10.04017
8	-11.00852
9	-11.93601
10	-12.82877
…	…

We're almost done, but it's going to be a bit hairy. The original problem was stated in terms of x, with the infinitely high barrier at x = 0 and the classical turning point at $x = x_m = E/F$. When we switched variables to w, the classical turning point, <u>the location of which depends on the energy of the particle</u>, was set to w = 0. From previous discussions, we know that the wave function must be zero at x = 0, which means that x = 0 must correspond to a zero Z_n of A(w). So,

[11] This may not seem very obvious. The chain rule relationship is $\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dw^2}\left(\frac{dw}{dx}\right)^2 + \frac{d\psi}{dw}\frac{d^2w}{dx^2}$, with the last term being zero in this example.

[12] Well known to mathematicians, anyway.

$$w = \left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(x - \frac{E}{F}\right).$$

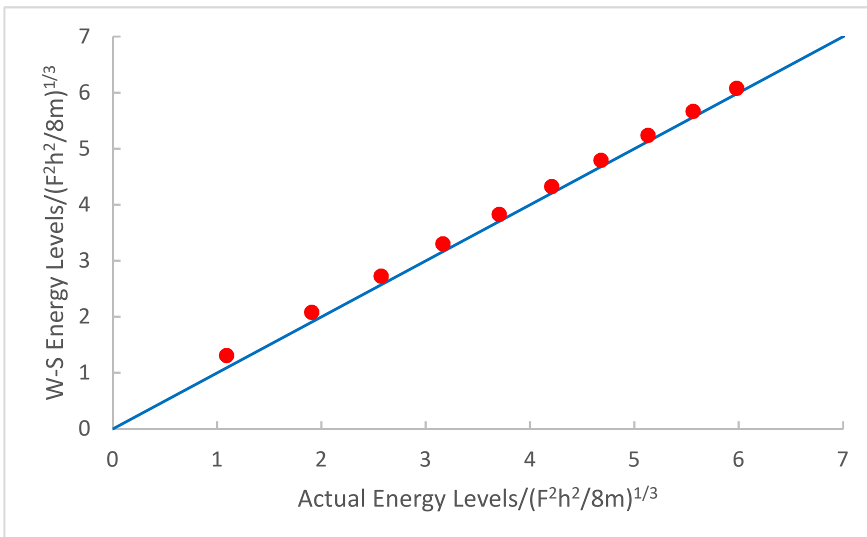
at x = 0 becomes

$$Z_n = \left(\frac{2mF}{\hbar^2}\right)^{1/3}\left(-\frac{E_n}{F}\right) \quad \rightarrow \quad E_n = -\left(\frac{\hbar^2F^2}{2m}\right)^{1/3} Z_n\,.$$

HOMEWORK 11-3

Consider a xenon atom bouncing against a hard surface, like a ball bouncing on the ground. What is the lowest allowed energy for such a situation? Assume that the atom's weight is the only force acting on the atom, other than the 'floor.'

For fun, let's compare the Schrödinger results here with those from the Wilson-Sommerfeld calculation. The energy levels are graphed in multiples of the quantity $(F^2h^2/8m)^{1/3}$. The blue line has slope one and is provided for comparison. We see that the agreement between the two calculations really isn't too bad, and gets better for higher values of n.



Now, some three dimensional examples. I'm going to be fairly detailed about the first one, even though the wave solutions and energy values results may be obvious to you; this is to 'get you in the mood' for the hydrogen atom, where those steps will be necessary.

Particle in a 3-d Box

Consider a rectangular box of edges L_x, L_y, and L_z, presumably all different. We'll assume that the stationary state solution is separable, i.e.,

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z).$$

In three dimensions, the Schrödinger equation with no potential energy inside the box will be

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\,\psi(x,y,z)$$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_x(x)\psi_y(y)\psi_z(z) = E\,\psi_x(x)\psi_y(y)\psi_z(z)$$
$$\frac{-\hbar^2}{2m}\left(\psi_y\psi_z\frac{\partial^2\psi_x}{\partial x^2}+\psi_x\psi_z\frac{\partial^2\psi_y}{\partial y^2}+\psi_x\psi_y\frac{\partial^2\psi_z}{\partial z^2}\right) = E\,\psi_x\psi_y\psi_z.$$

Here, I dropped the explicit dependences on x, y, and z for brevity. Now, let's divide both sides by $\psi_x\psi_y\psi_z$:

$$\frac{-\hbar^2}{2m}\left(\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2}+\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2}+\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2}\right) = E\,.$$

Now, since each term is a function only of its proper variable, the terms must individually be constant:

$$\frac{-\hbar^2}{2m}\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} = B_x$$
$$\frac{-\hbar^2}{2m}\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2} = B_y$$
$$\frac{-\hbar^2}{2m}\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2} = B_z\,,$$

with $B_x + B_y + B_z = E$. We've already solved these equations, above, for the one dimensional box.

$$\psi_{n_x}(x) = \sqrt{\frac{2}{L_x}}\,\sin\left(\frac{n_x\pi}{L_x}x\right) \quad B_{n_x} = n_x^2\frac{h^2}{8mL_x^2}$$

$$\psi_{n_y}(y) = \sqrt{\frac{2}{L_y}}\,\sin\left(\frac{n_y\pi}{L_y}y\right) \quad B_{n_y} = n_y^2\frac{h^2}{8mL_y^2}$$

$$\psi_{n_z}(z) = \sqrt{\frac{2}{L_z}}\,\sin\left(\frac{n_z\pi}{L_z}z\right) \quad B_{n_z} = n_z^2\frac{h^2}{8mL_z^2}\,,$$

or, recombining the parts, the particle's normalized wavefunction is

$$\psi(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x\pi}{L_x}x\right) \sin\left(\frac{n_y\pi}{L_y}y\right) \sin\left(\frac{n_z\pi}{L_z}z\right)$$

with energy

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{h^2}{8m}.$$

Of course, n_x, n_y, and n_z are positive integers.

Let's look at a special case, where L_x, L_y, and L_z are all equal to L, *i.e.*, a cube. Then, the allowed energy values become

$$E_{n_x,n_y,n_z} = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{h^2}{8mL^2}.$$

The lowest energy state is when all three n values are one: $E_{1,1,1} = 3h^2/8mL^2$. The next higher allowed energy is $3h^2/4mL^2$**,** but there are three distinct stationary states that possess that energy: (1, 1, 2), (1, 2, 1), and (2, 1, 1). These states are said to be *degenerate*.[13] What are the next few allowed energy values, and are the corresponding states degenerate or non-degenerate?

(1, 2, 2), (2, 1, 2), (2, 2, 1) $E = 9h^2/8mL^2$ three-fold degenerate
(3, 1, 1), (1, 3, 1), (1, 1, 3) $E = 11h^2/8mL^2$ three-fold degenerate
(2, 2, 2) $E = 3h^2/2mL^2$ non-degenerate
(3, 2, 1), (3, 1, 2), (2, 1, 3), (2, 3, 1), (1, 2, 3), (1, 3, 2) $E = 7h^2/4mL^2$ six-fold degenerate
(3, 2,2), (2, 3, 2), 2, 2, 3) $E= 17h^2/8mL^2$ three-fold degenerate
In the cube, degenerate states occur not only when the n-indices are mixed around; the states (7, 2, 1), (7, 1, 2), (2, 1, 7), (2, 7, 1), (1, 2, 7), (1, 7, 2), (6, 3, 3), (3, 6, 3), (3, 3, 6), (5, 5, 2), (5, 2, 5), and (2, 5, 5) all have the same energy and are therefor twelve-fold degenerate.

HOMEWORK 11-4

Calculate the energies of the first 15 energy levels for a rectangular box L×L×2L as multiples of $\frac{h^2}{8mL^2}$.

Harmonic Oscillator in 3-d

Next, let's briefly examine the three dimensional SHO, specifically, the energy levels. The method of solution is the same for the three dimensional box. In the end, we obtain

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[13] This is not to say that some energy levels for the original box couldn't be degenerate; it would depend on the ratios of L_x:L_y:L_z.

$$E_{n_x,n_y,n_z} = \left(n_x + \tfrac{1}{2}\right)\hbar\sqrt{\frac{C_x}{m}} + \left(n_y + \tfrac{1}{2}\right)\hbar\sqrt{\frac{C_y}{m}} + \left(n_z + \tfrac{1}{2}\right)\hbar\sqrt{\frac{C_z}{m}}\,.$$

Here, each n is 0, 1, 2, 3, … . If the oscillator is *isotropic*, or $C_x = C_y = C_z = C$, then

$$E_{n_x,n_y,n_z} = \left(n_x + n_y + n_z + \tfrac{3}{2}\right)\hbar\sqrt{\frac{C}{m}} = \left(n_x + n_y + n_z + \tfrac{3}{2}\right)\hbar\omega_o\,.$$

Our last example is a killer, mathematically: the hydrogen atom. We shall devote an entire section to it.

NOTE ONE

Let's rewrite the time independent Schrödinger equation this way:

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\,(U - E)\,\psi\,.$$

So, if $U \neq \pm\,\infty$, then the second derivative is well-defined, and the first derivative is continuous.

NOTE TWO

For now, take a look at the final Heisenberg uncertainty principle discussion.

NOTE THREE

Since

$$K = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}\,,$$

we expect

$$\hat{K} = \frac{-\,\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \frac{-\,\hbar^2}{2m}\,\nabla^2\,.$$

NOTE FOUR

For fun, let's compare these results with the classical approach. The probability density for the particle in a certain region of width Δx is proportional to the time it spends there, and that is inversely proportional to the particle's speed, and that in turn is related to the kinetic energy:

$$P(a < x < a + \Delta x) \sim \frac{1}{v} \sim \frac{1}{\sqrt{K}}\,,$$

which is of course the same value everywhere in the box, except during the brief turn-arounds. So, although it may be obvious, we'll normalize the probability density function

$$\int_0^L P(x)\,dx = 1 \quad \rightarrow \quad P(L - 0) = 1 \quad \rightarrow \quad P = \frac{1}{L}\,.$$

$$P(a < x < a + \Delta x) = \int_a^{a+\Delta x} P(x)\,dx = \int_a^{a+\Delta x} \frac{1}{L}\,dx = \frac{\Delta x}{L}\,.$$

Let's return to the quantum solution again. As n increases, the number of 'humps' in the wave function increases, making the probability density more evenly distributed. Keep in mind that the average of the sine squared function is half the amplitude, and each hump has height 2/L. If we were to average out the hills and valleys, as it were, the average value of the probability density would be ½ (2/L) = 1/L. So, we see that the quantum world begins to agree with the classical world as n gets large.