Chapter 6 Supplemental Material

1 Non-constant Potential Energies

You've seen that the basis function for the free particle (where the potential energy is zero over all space) and for the "particle in a box" (in problem 6.10, where the potential is zero from 0 to a and infinite every where else)[1] is e^{ikx}, or equivalently, $\sin(kx)$ and $\cos(kx)$. But what happens when the potential energy is not constant?

In one fundamental sense, nothing is different–you've seen that the Schrödinger equation can be derived from the energies of a sinusoidal wave, which means that sinusoidal functions will always be solutions. When the potential energy V is zero, the time-independent Schrödinger equation looks like

$$E\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}. \tag{1}$$

A single sinusoidal function $\psi(x) = \sin(kx)$ solves this differential equation:

$$E\sin kx = \frac{k^2\hbar^2}{2m}\sin kx, \tag{2}$$

when $k = \sqrt{\frac{2mE}{\hbar^2}}$, because the second derivative of $\sin(kx)$ is $-k^2\sin(kx)$. The functions cancel, and the equation becomes $E = E$.

Let's see what happens when you introduce a non-zero potential, such as $V(x) = ax$ and use the same sinusoidal wavefunction. The Schrödinger equation becomes

$$E\sin kx = \frac{k^2\hbar^2}{2m}\sin kx + ax\sin(kx). \tag{3}$$

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[1]The following discussion assumes you've worked through that problem or the online solutions, so if you haven't yet, now is a good time!

While the sine functions still cancel out, you're left with

$$E = \frac{k^2\hbar^2}{2m} + ax. \tag{4}$$

The total energy E should be constant, but here it depends on the position x.

Evidently, a single sine wave is not a good solution. Doesn't this contradict our earlier statement? No–*some* function is a good solution to this equation, and you can always write any function as a linear combination of sines (or cosines) using Fourier analysis. It's the appropriate combination of sines and cosines, or plane waves e^{ikx}, that will still solve this equation, not one individual wave.

If you want a single wavefunction (what we call the basis function) to solve the Schrödinger equation, that solution will depend on the form of the potential energy.

2 Quantum Harmonic Oscillator

As an example of a non-constant potential, let's look at the harmonic oscillator, an important system in quantum mechanics because it's the simplest model of chemical bonding. Both classically and in quantum mechanics, the harmonic oscillator is defined by a parabolic potential energy $V(x) = \frac{1}{2}m\omega^2 x^2$. The Schrödinger equation is

$$E\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\psi \tag{5}$$

You can find the derivation of solutions to the differential equation in quantum mechanics textbooks, so we will investigate what those solutions look like and compare to the constant potential energy case.

As with the particle in a box, the harmonic oscillator only allows for certain, quantized solutions $\psi_n(x)$. The functional form is more complex,

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(x')e^{-\frac{m\omega x^2}{2\hbar}}, \tag{6}$$

where $H_n(x')$ are the Hermite polynomials (listed in Table 2) and $x' \equiv \sqrt{\frac{m\omega}{\hbar}}x$.

Hermite Polynomials

$H_0(x') = 1$
$H_1(x') = 2x'$
$H_2(x') = -2 + 4x'^2$
$H_3(x') = -12x' + 8x'^3$

Take a moment, before worrying about the exact forms of $H_n(x')$, to consider what effect the Gaussian term $e^{-\frac{m\omega x^2}{2\hbar}}$ has on all harmonic oscillator basis wavefunctions. When x goes to $\pm\infty$, the Gaussian term goes to zero. This is very useful, because the potential energy $V(x) = \frac{1}{2}m\omega^2 x^2$ becomes infinite at $x = \pm\infty$; an infinite potential is a perfect barrier that does not allow the wavefunction to exist. So, you can see that Eq. 6 behaves correctly at the extreme limits.

Energies for the quantum harmonic oscillator are given by $E_n = (n + 1/2)\hbar\omega$; the lowest energy is $\hbar\omega/2$, when $n = 0$. Plugging in $H_0(x')$ into Eq. 6 gives the lowest energy wavefunction

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}, \tag{7}$$

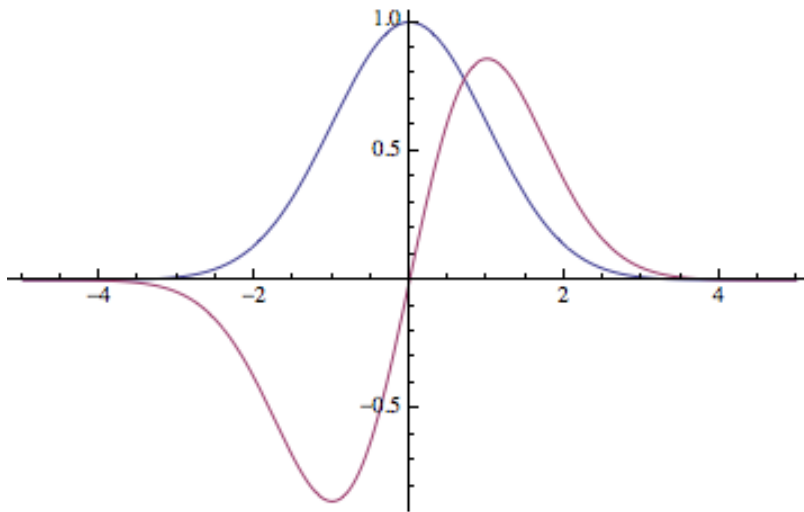which is simply a Gaussian function, as shown (with $\psi_1(x)$) in Fig. 1)

Figure 1: The lowest two energy wavefunctions for the harmonic oscillator, in units where $m = \omega = \hbar = 1$.

The next lowest energy, $3\hbar\omega/2$, occurs for $n = 1$. In this case the wavefunction picks up a factor of x from $H_1(x')$:

$$\psi_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}} \left(2\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}} \tag{8}$$

Simplifying constants gives

$$\psi_1(x) = Axe^{-\alpha x^2/2}, \tag{9}$$

where $A = \left(\frac{m\omega}{\pi\hbar}\right)^{3/4} 2\sqrt{2\pi}$ and $\alpha = \frac{m\omega}{\hbar}$. To demonstrate the earlier point, what is the Fourier analysis of $\psi_1(x)$? That is, what is the combination of plane waves that solves the harmonic oscillator Schrödinger equation?

According to Eq. 3.34 or 6.36, the wavefunction $\psi(x)$ is an integral of the wavenumber function $\phi(k)$. Our first step, then, is to find $\phi(k)$:

$$\begin{aligned}
\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi_1(x) e^{-ikx} dx \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} Axe^{-\alpha x^2/2 - ikx} dx \\
&= -ik\alpha^{-3/2} e^{-k^2/(2\alpha)},
\end{aligned}$$

where the integral can be evaluated with your favorite mathematical software.

The wavenumber function is actually similar to the spatial wavefunction (it goes as ke^{-k^2}), but it's picked up a factor of i. This i has implications for the spatial wavefunction $\psi(x)$, because you find $\psi(x)$ by integrating $\phi(k)$ multiplied by e^{ikx}. Think about expanding with the Euler equation: $e^{ikx} = \cos(kx) + i\sin(kx)$. We know that the original function is real, so the final wavefunction, composed of plane waves must also be real. Multiplying by i means the real part of $\phi(x)$ will be the sines instead of cosines. This is consistent with the graph of $\psi(x)$, which, like sine, is an odd function.

The wavefunction $\psi_1(x)$ can now be written as the Fourier transform of the wavenumber function:

$$\psi_1(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(\frac{-ik}{\alpha^{3/2}}\right) e^{-k^2/(2\alpha)} e^{ikx} dk. \tag{10}$$

Fig. **2** shows this integral, evaluated from $k = $ -1 to 1, -2 to 2, and -10 to 10, compared to the actual function. Even though 10 is not infinity, the last integral is indistinguishable from the original wavefunction; this happens because $\phi(k)$ is relatively well-condensed around 0 and bigger values of k do not contribute much.
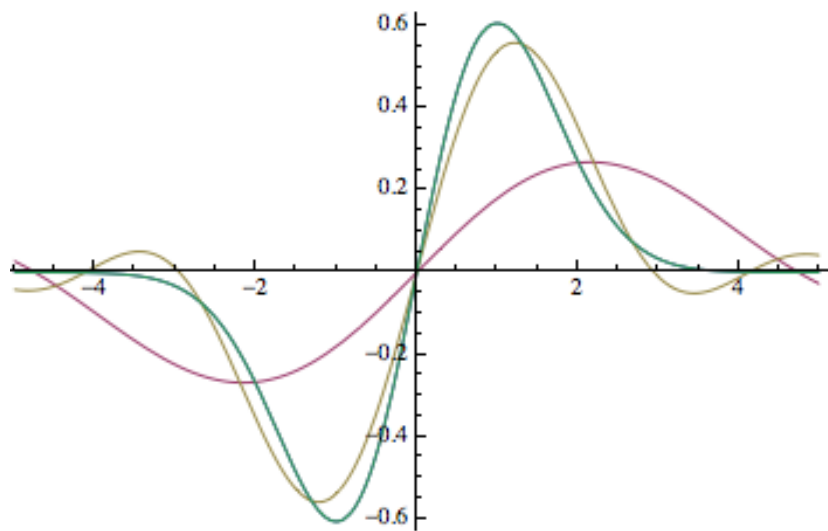
Figure 2: The wavefunction for the second lowest energy level in the harmonic oscillator and its representation as the integral of the wavenumber function. The wavenumber function is integrated over the bounds ±1, ±2, and ±10.