The harmonic oscillator

Recall from classical physics that a mass on a spring, \( F = -kx \), moves with simple harmonic motion.

\[
F = -kx \implies U = \frac{1}{2}kx^2 \quad \text{and SHO with} \quad \omega = \sqrt{\frac{k}{m}}
\]

We can solve the "motion" (wavefunction) of such a potential with Schrödinger's equation. It is in fact a fairly good approximation for several real systems like diatomic molecules.

So,

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}k'x^2\psi = E\psi
\]

where I'm calling the "spring constant" \( k' \) to distinguish it from wave number.

I won't discuss how one finds the solution to this, just state it.

\[\psi(x) = Ae^{-ax^2}\]

And, as usual we can find \( A \) and \( a \) by algebra and boundary conditions.
\[
\frac{d\psi}{dx} = -2a x A e^{-ax^2} \\
\frac{d^2\psi}{dx^2} = -2a A e^{-ax^2} + 4a^2 x^2 A e^{-ax^2}
\]

So plugging in,

\[
-\frac{\hbar}{2m} \left( -2a A e^{-ax^2} \right) - \frac{\hbar^2}{2m} 4a^2 x^2 A e^{-ax^2} + \frac{1}{2} k' x^2 A e^{-ax^2} = E A e^{-ax^2}
\]

cancel the $A e^{-ax^2}$ and

\[
\frac{\hbar^2 a}{2m} - E + \frac{2\hbar^2}{m} a^2 x^2 + \frac{1}{2} k' x^2 = 0
\]

Note that this is not an equation that we should solve for $x^2$. Rather, it is one that must be true for all $x$. So,

\[
\frac{\hbar^2 a}{2m} = E \quad \text{AND} \quad \frac{2\hbar^2 a^2}{m} = \frac{1}{2} k'
\]

\[
\Rightarrow a = \sqrt{\frac{k' m}{2\hbar}}
\]

and

\[
E = \frac{\hbar^2 \sqrt{k' m}}{4 m/\hbar} = \frac{1}{2} \hbar \sqrt{\frac{k'}{m}}
\]
Identifying $\sqrt{k/m}$ as $\omega$ as usual, we get

$$E = \frac{1}{2} \hbar \omega$$

The wave function is then

$$\psi(x) = A e^{-\alpha x^2} = A e^{-\frac{\sqrt{k/m} x^2}{\hbar}}$$

We can find $A$ by normalizing the wavefunction to have

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} |A|^2 e^{-\frac{\sqrt{k/m} x^2}{\hbar}} \, dx = 1$$

This is left as a homework exercise, and it is trivial since it is just calculus that can be helped with an integral table.

Note, when we plot this, $\psi$ extends into Euclidean region. That is new! We'll see more about this later.
These were for the lowest energy state.

\[ E_0 = \frac{1}{2} \hbar \omega \quad \psi = A e^{-\sqrt{\kappa m \omega/\hbar} x^2} \]

Another, higher energy, solution is

\[ \psi_n(x) = f_n(x) e^{-\alpha x^2} \]

where \( f_n \) is the \( n \)th order polynomial.

\[ E_n = (n+\frac{1}{2}) \hbar \omega. \]

\[ \text{etc.} \]

\[ P(x) = \psi^* \psi \]

is bigger toward the edges as expected classically since the particle is moving slowly there.

Then, time dependence is given by

\[ \Phi(x, t) = \psi(x) e^{-iE \hbar \frac{t}{\hbar}} \]
A particle in a finite well

We considered an infinite well, which corresponds to \( U = \infty \) outside the box. What if \( U \) is not infinite?

\[ U(x) = \begin{cases} 
0 & \text{if } x < L \\
U_0 & \text{otherwise}
\end{cases} \]

This is a more realistic model of an atom since it can be "ionized" if \( E > U_0 \).

What is the wavefunction for a particle in such a potential well? What are its energy levels?

The answers come by solving the Schrödinger equation with this \( U(x) \) and boundary conditions.

For \( 0 < x < L \) we have the same as before:

\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E \psi(x) \quad \text{since } U(x) = 0. \]

\[ \Rightarrow \psi(x) = Ae^{ikx} + Be^{-ikx} \]
\[ \psi(x) = A e^{ikx} + B e^{-ikx} \]

\[ \frac{\partial \psi}{\partial x} = ik A e^{ikx} - ik B e^{-ikx} \]

\[ \frac{\partial^2 \psi}{\partial x^2} = -k^2 A e^{ikx} - k^2 B e^{-ikx} = -k^2 \psi(x) \]

So,

\[ -\frac{k^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = (E - U) \psi \]

\[ \Rightarrow \frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} (E - U) \psi \]

\[ -k^2 \psi = -\frac{2m}{\hbar^2} (E - U) \psi \]

\[ k = \sqrt{2m(E-U)} / \hbar \]

If \( U = 0 \), then we just get \( k = \frac{\sqrt{2mE}}{\hbar} \) as before, and \( \psi(x) \) is the \( \sin \) and \( \cos \) combination.

If \( U = U_0 > 0 \), then \( k = \frac{\sqrt{2m(E-U_0)}}{\hbar} = i \frac{\sqrt{2m(U_0-E)}}{\hbar} \)

and \( \psi(x) = Ae^{-\sqrt{2m(U_0-E)}x/\hbar} + Be^{\sqrt{2m(U_0-E)}x/\hbar} \)

which is exponential decay, not oscillation!

Same form, but very different meaning inside and outside the box. To be general, we need to allow different coefficients outside the box:

\[ \psi(x) = Ce^{-\sqrt{2m(U_0-E)}x/\hbar} + De^{\sqrt{2m(U_0-E)}x/\hbar} \]
And, to make the wavefunction stay finite, we need $C = 0$ for $x < 0$ and $D = 0$ for $x > L$.

$$
\psi(x) = \begin{cases} 
\frac{\sqrt{2m(E-V_0)}}{\pi} & \text{for } x < 0 \\
A e^{i \frac{\sqrt{2mE} x}{\hbar}} + B e^{-i \frac{\sqrt{2mE} x}{\hbar}} & \text{for } 0 < x < L \\
C e^{-i \frac{\sqrt{2m(E-V_0)} x}{\hbar}} & \text{for } x > L
\end{cases}
$$

The boundary conditions require that $\psi$ is continuous, so

$$
D = A + B
$$

and $C$ is related to $A$ and $B$ to $L$, but the algebra will get really messy. So, instead of plodding through it, let's look at the solution graphically.

![Graphical representation of the wavefunction](image)
What are the energy levels?
Finding them is even messier than finding the wavefunctions. However, we can say how they are found: values of $E$ for which a sine wave like $e^{i \sqrt{2mE} x / \hbar}$ matches an exponential like $e^{i \sqrt{2m(U_0 - E)} x / \hbar}$ at $x = 0 \leq L$.

As described in YE, we can compare the energy levels on a finite wall to an infinite wall of the same width, $E$, is always less.
Note that $E \propto \frac{1}{L^2}$ which came from the de Broglie wavelength.

So, we can calculate an approximate size for an atom by modeling it approximately as a box.

$$13.6\text{eV} \approx 10\text{eV} = \frac{n^2\hbar^2}{2amL^2}$$

$$\Rightarrow L \approx \sqrt[2]{\frac{10\text{eV}}{2am}}$$

$$L = \frac{6 \times 10^{-34} \text{J} \cdot \text{s}}{\sqrt{2.9 \times 10^{-31} \text{kg} \cdot 10\text{eV} \cdot 1.6 \times 10^{-19} \text{J}}}$$

$$\approx \frac{3 \times 10^{-34}}{10 \sqrt{2.10 \cdot 10^{-10} \cdot 1.5 \cdot 10^{-50}}} = \frac{3 \times 10^{-34}}{10 \sqrt{3} \cdot 10^{-59}}$$

$$= \frac{\sqrt{3}}{10} \cdot 10^{-9}$$

$$= 0.1 \times 10^{-9} \approx 0.1\text{nm}$$
Similarly, we can estimate the size of the nucleus since it gives off $\gamma$-rays with energies of $\sim 10$ MeV.

$$E \rightarrow 10^6 \times E$$

$$\Rightarrow L \rightarrow 10^{-3} L$$

(The masses also change by about 1000, so

$$L \rightarrow \frac{1}{10^6 \times 10^3} L = \frac{1}{10^{10}} L$$

$\sim 10^{-4}$ or $10^{-5}$ of an atom.

$0.1 \text{ nm} \rightarrow \sim 1 \text{ fm}$.

These are of course approximations, but correct to about the right order of magnitude.