Schrödinger's Equation – 2
The Simple Harmonic Oscillator

Example: The simple harmonic oscillator
Recall our rule for setting up the quantum mechanical problem: "take the classical potential energy function and insert it into the Schrödinger equation." We are now interested in the time independent Schrödinger equation.

We write the classical potential energy as

$$V(x) = \frac{1}{2} m\omega^2 x^2 ,$$

where the classical solutions are

$$x(t) = A\cos\omega t + B\sin\omega t .$$

This indicates that the ω we have used in the potential energy corresponds to the classical angular frequency of the oscillator. You should understand why the mass *m* has appeared in the potential energy in this description. The time independent Schrödinger equation that we wish to solve is thus:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x) .$$

Preliminary to solution
The first step in attempting a solution of this equation is to "tidy up" the variables by removing all unnecessary quantities, possibly by transforming to new variables. Let's first write the equation in "normal form":

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \left\{\frac{2m}{\hbar^2}E - \frac{m^2\omega^2}{\hbar^2}x^2\right\}\psi(x) = 0 .$$

Now $m^2\omega^2/\hbar^2$ has the dimensions of length^{-4} and $2mE/\hbar^2$ has the dimensions of length^{-2}. We thus introduce a length parameter *a* defined by

$$a = \sqrt{\frac{\hbar}{m\omega}}$$

which facilitates the definition of a dimensionless length *y* and a dimensionless energy ε through

$$x = ya$$

$$E = \varepsilon\hbar\omega/2,$$

This enables us to write the Schrödinger equation in the simplified form

$$\frac{d^2\psi}{dy^2} + (\varepsilon - y^2)\psi = 0 .$$

This equation cannot be solved in terms of the standard functions. It would be possible to proceed from here by looking for a power series solution, using the techniques we have learned. However it proves beneficial to stop and think and examine requirements which physically allowed solutions to the equation must satisfy.

Limiting behaviour

When considering the quantum mechanical particle in a box you will recall that the confining potential of the box walls ensured that the wave function vanished outside the box and on its walls. Now a particle in a harmonic oscillator potential is not subject to such constraints. But it is confined by the oscillator potential; it becomes increasingly difficult to move the particle further and further from the centre of the well. So far as the wave function is concerned, and the interpretation of its modulus squared as a probability, it is clear that ψ must decrease as *y* becomes larger and larger.

In the limit of large *y*, that is, when

$$y >> \sqrt{\varepsilon}$$

it is clear that ε may be ignored in the above equation. This is saying that when *y* is very large the form of the wave function is independent of its energy eigenvalue. In this limit the equation simplifies to

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0 .$$

This equation also cannot be solved in terms of the standard functions. However what we are interested in is the limiting behaviour of the solution at large *y*. It is easy to check that the function $e^{-y^2/2}$ satisfies the equation in this limit.

⌈In fact you can show quite easily that

$$\left(\frac{d^2}{dy^2} - y^2\right) e^{-y^2/2} = e^{-y^2/2},$$

which vanishes as $y \to \infty$. ⌋

Our conclusion is that the physically allowed solutions must satisfy the requirement

$$\psi(y) \sim e^{-y^2/2} \qquad \text{as} \qquad y \to \infty .$$

This is a form of *boundary condition*; you should appreciate how this is an extension of the idea of the boundary condition on a particle in a box.

Exploiting the boundary condition

We incorporate this boundary condition into our solution by writing a full solution as

$$\psi(y) = H(y)e^{-y^2/2} .$$

The clever thing about this is that the function $H(y)$ must not overwhelm the $e^{-y^2/2}$ behaviour at large *y*, so $H(y)$ must only be a polynomial in *y*; its power series *must* terminate.

By substituting this product solution into the equation for $\psi(y)$ we obtain the equation obeyed by the new function *H*(*y*):

$$\frac{\mathrm{d}^2H}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}H}{\mathrm{d}y} + (\varepsilon - 1)H = 0.$$

This is Hermite's equation.

Solutions of Hermite's equation

Hermite's equation cannot be solved in terms of elementary functions. We shall look for series solutions. We assume a simple series of the form

$$H(y) = \sum_{i=0}^{\infty} a_i y^i$$

so that the derivatives are

$$\frac{\mathrm{d}H}{\mathrm{d}y} = \sum_i i a_i y^{i-1}$$

$$\frac{\mathrm{d}^2H}{\mathrm{d}y^2} = \sum_i i(i-1) a_i y^{i-2}.$$

We substitute these into Hermite's equation, to give

$$\sum_i i(i-1) a_i y^{i-2} - 2y\sum_i i a_i y^{i-1} + (\varepsilon - 1)\sum_i a_i y^i = 0.$$

The next step is to incorporate the *y* factor in the second term into the sum and increase the index *i* by 2 in the first term so that the equation simplifies to

$$\sum_i \left\{(i+2)(i+1)a_{i+2} + \left[-2i + (\varepsilon - 1)\right]a_i\right\} y^i = 0.$$

As we have argued previously, for the expression on the left hand side to be identically zero, each power of *y* must be zero. In other words

$$(i+2)(i+1)a_{i+2} + \left[-2i + (\varepsilon - 1)\right]a_i = 0$$

or

$$a_{i+2} = \frac{2i - \varepsilon + 1}{(i+1)(i+2)} a_i,$$

a recurrence relation for the coefficients.

Since the series has been defined to start at $i = 0$ it follows that a_{-1} and a_{-2} are zero, so that the lowest order non-vanishing coefficients are a_0 and a_1. These will be independent constants since the recurrence relation connects alternate terms.

We now proceed to build up the coefficients of the power series in the usual way.

Even powers

We start with $i = 0$ which we substitute into the recurrence relation:

$$a_2 = \frac{1 - \varepsilon}{2} a_0.$$

Next set $i = 2$

$$a_4 = \frac{5-\varepsilon}{4\times 3}a_2$$
$$= \frac{(1-\varepsilon)(5-\varepsilon)}{4!}a_0.$$

Next set $i = 6$

$$a_6 = \frac{9-\varepsilon}{6\times 5}a_0$$
$$= \frac{(1-\varepsilon)(5-\varepsilon)(9-\varepsilon)}{6!}a_0.$$

The general term, for even *i* is given by

$$a_i = \frac{(1-\varepsilon)(5-\varepsilon)(9-\varepsilon)\ldots(2i+1-\varepsilon)}{i!}a_0.$$

Odd powers

Now we start with $i = 1$ which we substitute into the recurrence relation

$$a_3 = \frac{3-\varepsilon}{3!}a_1.$$

Next set $i = 3$

$$a_5 = \frac{7-\varepsilon}{5\times 4}a_3$$
$$= \frac{(3-\varepsilon)(7-\varepsilon)}{5!}a_0.$$

The general term, for odd *i* is given by

$$a_i = \frac{(3-\varepsilon)(7-\varepsilon)\ldots(2i+1-\varepsilon)}{i!}a_1.$$

Termination of the series – energy quantisation

We have argued that the boundary condition requirement on the wave function $\psi(y) = H(y)e^{-y^2/2}$ is that for sufficiently large *y* the exponential term dominates. The function $H(y)$ must not overwhelm the exponential so it can be, at most, a polynomial – a terminating power series. The n^{th} term of the series will vanish if

$$2n+1-\varepsilon = 0$$

and this holds whether *N* is odd or even.

Here *n* is a positive integer (or zero). It is clear that the series will only terminate for specific values of ε. These are the allowed energy values for the system – the energy *eigenvalues*. We may write this condition (on the dimensionless energy) as

$$\varepsilon = 2n+1 \qquad n = 0, 1, 2, 3, \ldots$$

For the actual energy *E* this gives the result

$$E = (2n+1)\frac{\hbar\omega}{2}$$

or

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

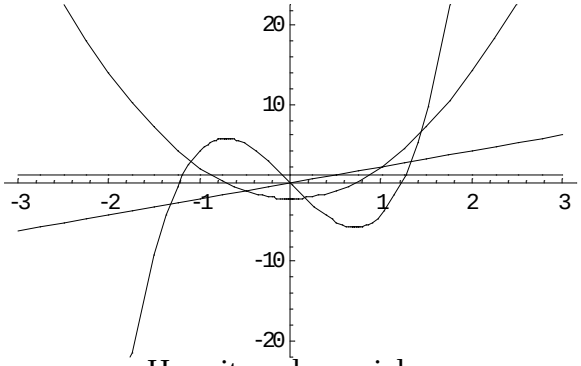
We see that the energy eigenvalues are *equally spaced*; this is a special property of the simple harmonic oscillator.

Hermite polynomials

The series solutions corresponding to the eigenvalues, that is the *eigenfunctions*, are polynomials. The polynomials $H(y)$ corresponding to the different *n* are called *Hermite polynomials*, denoted by $H_n(y)$. The first few Hermite polynomials (conventionally normalised) are

$$H_0(y) = 1 \qquad H_1(y) = 2y$$
$$H_2(y) = 4y^2 - 2 \qquad H_3(y) = 8y^3 - 12y$$

The figure shows these



Hermite polynomials

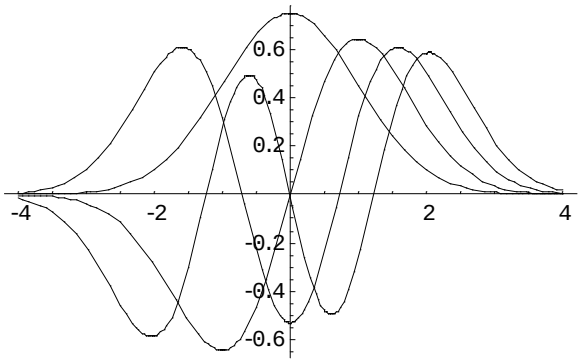
The harmonic oscillator wave functions are then given by

$$\psi_n(y) = H_n(y)e^{-y^2/2}.$$

In terms of real distance $x = ya$, this is

$$\psi_n(x) = H_n(x/a)e^{-x^2/2a^2}.$$

The first four wave functions, corresponding to the Hermite polynomials above are plotted below.



Harmonic oscillator wave functions

Orthogonality
The Hermite polynomials are orthogonal. In considering orthogonality there are three important things to know:

1 the orthogonality *interval*

2 the *weight finction* (if any)

3 the *norm.*

The orthogonality interval is the range over which orthogonal function expansions "work" before repeating or something. Recall what happens to Fourier series outside their range. The orthogonality integral is evaluated between the limits specified by the orthogonality inteval. For Hermite polynomials the interval is $-\infty$ to ∞.

The weight function for the Hermite polynomials is e^{-y^2}. Thus the orthogonality integral is written

$$\int_{-\infty}^{\infty} e^{-y^2} H_n(y) H_m(y)\,\mathrm{d}y = 0 \quad \text{when} \quad m \neq n\,.$$

You should see that the weight function in this integral indicates that the harmonic oscillator wave functions $\psi_n(y) = H_n(y)e^{-y^2/2}$ are orthogonal with a unit weight function.

The norm is the value of this integral when $m = n$. It is a non-trivial matter to show that the norm integral is given by

$$\int_{-\infty}^{\infty} e^{-y^2} H_n^2(y)\,\mathrm{d}y = 2^n \pi^{1/2} n!$$

Normalisation of the harmonic oscillator wave functions
Thus far we have not considered the normalisation of the wave functions. The square of the modulus of the wave function is a probability:

$$\left|\psi(x)\right|^2 \mathrm{d}x = p(x)\mathrm{d}x$$

is the probability of finding the particle in the range x to $x + \mathrm{d}x$. Since the probability of finding the particle *somewhere* must be unity, this gives the normalisation condition

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

So if we write the normalised harmonic oscillator wave function as

$$\psi_n(x) = AH_n(x/a)e^{-x^2/2a^2}$$

then normalisation requires

$$A^2 \int_{-\infty}^{\infty} H_n^2(x/a)e^{-x^2/a^2} \,\mathrm{d}x = 1 .$$

The integral is essentially the norm integral for the Hermite polynomial orthogonality:

$$\begin{aligned} \int_{-\infty}^{\infty} H_n^2(x/a)e^{-x^2/a^2} \,\mathrm{d}x &= a\int_{-\infty}^{\infty} H_n^2(y)e^{-y^2} \,\mathrm{d}y \\ &= 2^n \pi^{1/2} an! \end{aligned}$$

so that

$$A = \left(2^n \pi^{1/2} an!\right)^{-1/2}$$

and the normalised harmonic oscillator wave functions are thus

$$\psi_n(x) = \left(2^n \pi^{1/2} an!\right)^{-1/2} H_n(x/a)e^{-x^2/2a^2} .$$

In fact the SHO wave functions shown in the figure above have been normalised in this way.

Classical limit of the quantum oscillator

A particle in a quantum harmonic oscillator in the ground state has a gaussian wave function. That means it is more likely to be found at the centre of the well. By contrast a particle in a classical harmonic oscillator will be more likely to be found at the extremes of its trajectory, where its velocity is smallest, and it spends least time at the centre where it is moving fastest. The Correspondence Principle says that in the limit of large quantum numbers the behaviour of a quantum system should approach that of the corresponding classical system. We can investigate this.

Classical Probabilities

A classical particle has a well-defined trajectory $x(t)$. This function can be differentiated, giving the velocity as a function of time. In quantum mechanics one cannot know both position and velocity simultaneously. In other words in quantum mechanics one cannot talk of a particle's trajectory. In quantum mechanics all one has is the wave function $\psi(x)$.

We want to compare the classical and the quantum harmonic oscillator. We shall do this by considering the classical analogue of the wave function; actually we will consider the analogue of $|\psi(x)|^2$.

In the quantum case we know that $|\psi(x)|^2$ is the probability of finding the particle in the range x to $x + \mathrm{d}x$. In the classical case, where we know the trajectory function $x(t)$ we can calculate the corresponding probability in the following way.

The probability of finding the particle in the range x to $x + \mathrm{d}x$ is proportional to the time $\mathrm{d}t$ the particle spends in the range x to $x + \mathrm{d}x$. And to normalise this probability we must divide by the time it takes to traverse all x values: that is, *half* the period. Since the velocity v is the time derivative of x

$$v = \frac{\mathrm{d}x}{\mathrm{d}t}$$

we can write $\mathrm{d}t$ as

$$\mathrm{d}t = \frac{\mathrm{d}x}{v}.$$

We wish to obtain $\mathrm{d}t$ as a function of x so all we require is to express the velocity in terms of the displacement:

$$\mathrm{d}t = \frac{\mathrm{d}x}{v(x)}.$$

Then we divide by π / ω to obtain a correctly normalised probability.

$$p(x) = \frac{\omega}{\pi v(x)}.$$

We can write the trajectory of the classical oscillator as

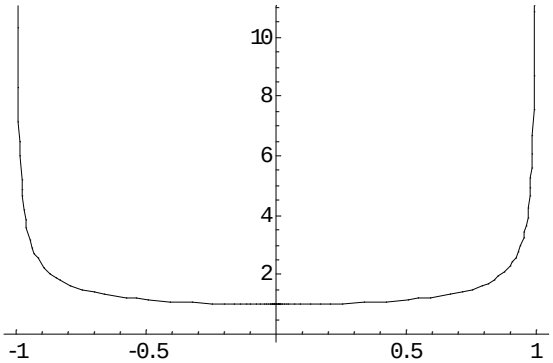
$$x(t) = x_0 \sin \omega t$$

where x_0 is the amplitude of the oscillations. Then the velocity is

$$v = \frac{\mathrm{d}x}{\mathrm{d}t} = x_0 \omega \cos \omega t$$
$$= \omega \sqrt{x_0^2 - x^2}.$$

From this we can express the classical SHO probability function as

$$p(x) = \frac{1}{\pi \sqrt{x_0^2 - x^2}}.$$



Probability function for the classical harmonic oscillator

(You should check the classical probability function is correctly normalised.)

Observe this is greatest at the extremities of the motion where the velocity goes to zero and it is smallest at the centre where the particle is moving fastest.

Now the classical oscillator has a well-defined amplitude; the displacement *x* can never be greater than the amplitude x_0. By contrast the wave function of quantum harmonic oscillator has (gaussian) tails which extend (in principle) off to infinity.

Quantum – classical connection

The quantum wave function for the harmonic oscillator has been shown to be

$$\psi_n(x) = \left(2^n \pi^{1/2} an!\right)^{-1/2} H_n(x/a) e^{-x^2/2a^2}$$

so the quantum probability function (in the state *n*) is then

$$\begin{aligned} p_n(x) &= \left|\psi_n(x)\right|^2 \\ &= \left(2^n \pi^{1/2} an!\right)^{-1} H_n^2(x/a) e^{-x^2/a^2}. \end{aligned}$$

To make connection with the classical probability function it makes sense to express the amplitude x_0 of the classical oscillator in terms of its energy.

Now

$$E = \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2.$$

And if we write the displacement as

$$x(t) = x_0 \sin(\omega t)$$

then

$$v(t) = \frac{\mathrm{d}x}{\mathrm{d}t} = x_0 \omega \cos(\omega t).$$

Thus the energy is given by

$$\begin{aligned} E &= \frac{1}{2}mx_0^2\omega^2 \cos^2(\omega t) + \frac{1}{2}mx_0^2\omega^2 \sin^2(\omega t) \\ &= \frac{1}{2}mx_0^2\omega^2. \end{aligned}$$

Then the amplitude is related to the oscillator energy

$$x_0^2 = \frac{2E}{m\omega^2}.$$

But since the energy of the oscillator is related to the quantum number *n* by $E = (n + 1/2)\hbar\omega$ we can express the amplitude in terms of *n* as

$$\begin{aligned} x_0^2 &= \frac{(2n+1)\hbar}{m\omega} \\ &= (2n+1)a^2 \end{aligned}$$

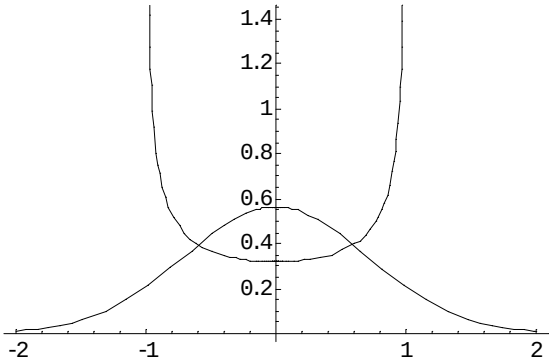
where *a* is the SHO length parameter introduced previously. The classical probability is then

$$p_n(x) = \frac{1}{\pi\sqrt{(2n+1)a^2 - x^2}},$$

while the quantum probability function is

$$p_n(x) = \left(2^n \pi^{1/2} an!\right)^{-1} H_n^2(x/a) e^{-x^2/a^2}.$$

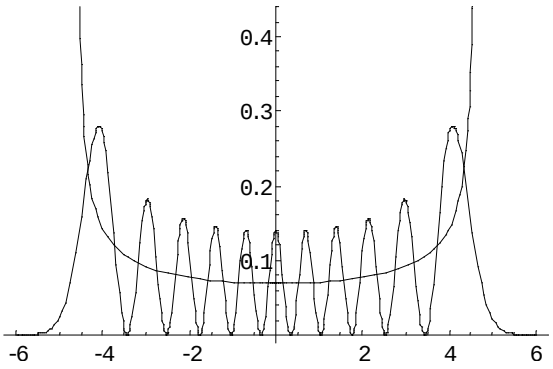
To compare these two, first let's plot the quantum ground state $(n = 0)$ and the classical analogue. As expected the two look completely different.



Quantum oscillator in the ground state compared with classical behaviour

This tells us that quantum mechanics gives behaviour very different from that expected from classical mechanics. But we know that the correspondence principle implies that one should get good agreement when *n* is large.

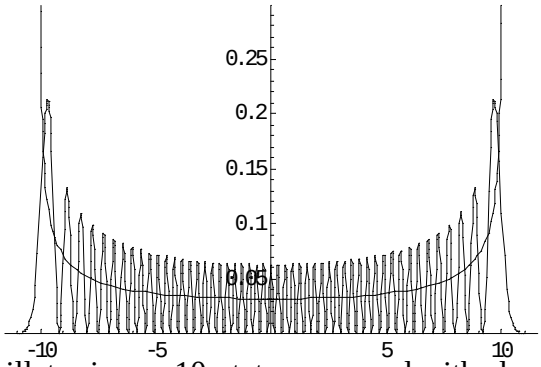
Now let's consider the case where the oscillator is in its 10^{th} excited state: $n = 10$.



Quantum oscillator in $n = 10$ state compared with classical behaviour

The quantum probability oscillates, but its does seem to peak at the extremities. And the mean of the oscillations seems to agree fairly well with the classical curve.

Now let us consider the behaviour when *n* is very large, when the correspondence principle should really be operating. We take $n = 50$ (we can't take *n* too large or the oscillations in the quantum probability will not be resolved by the printer).



Quantum oscillator in $n = 10$ state compared with classical behaviour

Now it is quite clear that the mean behaviour of the quantum oscillator is tending towards the classical limit.