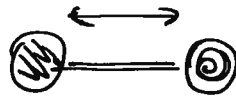


Energy Spectrum: Harmonic Oscillator

For our next example, I would like to discuss the quantum harmonic oscillator. The harmonic oscillator has a very important role in quantum mechanics, as it does in classical mechanics. First, just as in classical physics, almost every mechanical system has a “spherical cow” approximation that is equivalent to a harmonic oscillator. The exact solution of this problem gives insight into the physics of the full problem. A specific example occurs in the study of diatomic molecules such as O_2 . These molecules have a particular set of quantum energy levels associated with vibrations of the bond length.



Second, every mode of an electromagnetic wave in space is formally described by a harmonic oscillator. The quantum theory of the harmonic oscillator will eventually tell us how to quantize the electromagnetic field.

For the moment, I would like to solve the quantum harmonic oscillator in its simplest form. We consider the Schrödinger equation with the potential

$$V = \frac{1}{2} m \Omega^2 x^2$$

The classical problem is described by a Hamiltonian energy formula

$$E = \frac{p^2}{2m} + \frac{1}{2} m \Omega^2 x^2$$

The classical equations of motion are

$$\dot{x} = \frac{p}{m} \quad \dot{p} = -m\Omega^2 x$$

or

$$\ddot{x} = -\Omega^2 x$$

The classical solutions are sinusoidal oscillations

$$x(t) = A \sin(\Omega t + \phi)$$

The quantum problem is described by the time-independent Schrödinger equation

$$E\psi(x) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\Omega^2 x^2 \right] \psi(x)$$

The methods used in the previous lecture indicate that this is a problem with discrete spectrum only. First, consider solving this equation when $|x|$ is very large. We can ignore E and also drop other terms in which x appears to a smaller power than x^2 . Then the equation that we need to solve is

$$\frac{d^2}{dx^2} \psi \approx \frac{m^2 \Omega^2 x^2}{\hbar^2} \psi$$

The solutions

$$\psi(x) = \exp\left[\pm \frac{1}{2} \left(\frac{m\Omega}{\hbar} \right) x^2 \right]$$

solve the equation to the leading power of x . Then the most general solution of the Schrödinger equation behaves as $x \rightarrow \infty$ as

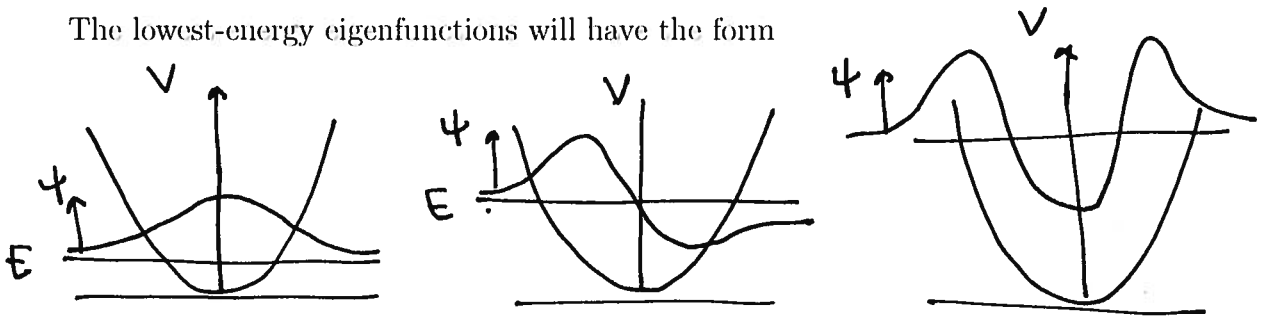
$$\psi(x) \sim C(E) e^{+\frac{1}{2} \frac{m\Omega}{\hbar} x^2} + D(E) e^{-\frac{1}{2} \frac{m\Omega}{\hbar} x^2}$$

Any solution with $C \neq 0$ has incorrect boundary conditions at infinity. This is the generic situation. However, as we saw in the previous lecture, we can integrate the Schrödinger equation starting from a solution that behaves as

$$\psi(x) \sim e^{-\frac{1}{2} \frac{m\Omega}{\hbar} x^2}$$

as $x \rightarrow -\infty$ and look for discrete energies E_i where $C(E_i) = 0$. These E_i are the discrete eigenvalues.

The lowest-energy eigenfunctions will have the form



These functions will be alternately *even* and *odd* under $x \rightarrow -x$, as required by the theorem that we proved in the previous lecture. The eigenfunctions will have 0, 1, 2, ... zeros, with the zeros of each function interleaving the zeros of the previous one.

We will now find these solutions explicitly. It is convenient to define

$$\xi = \left(\frac{m\Omega}{\hbar} \right)^{\frac{1}{2}} x$$

The units of the various factors are

$$\hbar \sim \frac{p}{k} \sim \frac{\text{kg m/sec}}{1/m} \sim \text{kg m}^2/\text{sec}$$

$$m\Omega \sim \text{kg/sec}$$

so the prefactor in ξ has the dimensions of $1/m$ and thus ξ is dimensionless. In terms of ξ , the Schrödinger equation becomes

$$E\psi = \left[-\frac{\hbar^2}{2m} \frac{m\Omega}{\hbar} \frac{\partial^2}{\partial \xi^2} + \frac{1}{2} m\Omega^2 \frac{\hbar}{m\Omega} \xi^2 \right] \psi$$

or

$$E\psi = (\hbar\Omega) \left[-\frac{1}{2} \frac{\partial^2}{\partial \xi^2} + \frac{1}{2} \xi^2 \right] \psi$$

Let

$$\epsilon = E/\hbar\Omega$$

This is also a dimensionless quantity. The Schrödinger equation can be rewritten as

$$\frac{\partial^2}{\partial \xi^2} \psi = (\xi^2 - 2\epsilon) \psi$$

To begin, we can try to solve this equation by

$$\psi(\xi) = e^{-\frac{1}{2}\xi^2}$$

Computing

$$\frac{\partial}{\partial \xi} \psi = -\xi e^{-\frac{1}{2}\xi^2}$$

$$\frac{\partial^2}{\partial \xi^2} \psi = (-1 + \xi^2) e^{-\frac{1}{2}\xi^2}$$

we find

$$\frac{\partial^2}{\partial \xi^2} \psi = (\xi^2 - 1) \psi$$

so this function satisfies the eigenvalue problem with

$$\epsilon = \frac{1}{2}$$

This simple solution is of exactly the right form to be the lowest energy eigenfunction sketched above.

To look for more eigenfunctions, we can assume that the solutions are of the form

$$\psi(\xi) = h(\xi) e^{-\frac{1}{2}\xi^2}$$

Then

$$\frac{\partial \psi}{\partial \xi} = (h' - \xi h) e^{-\frac{1}{2}\xi^2}$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = (h'' - 2\xi h' - h + \xi^2 h) e^{-\frac{1}{2}\xi^2}$$

The equation now becomes

$$h'' - 2\xi h' + (\xi^2 - 1)h = (\xi^2 - 2\epsilon)h$$

or

$$h'' - 2\xi h' + (2\epsilon - 1)h = 0$$

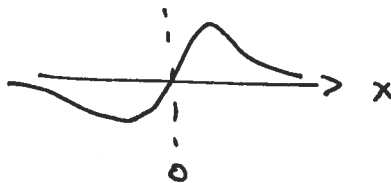
The function

$$h_0(\xi) = 1$$

satisfies this with $\epsilon = \frac{1}{2}$. Similarly,

$$h_1(\xi) = \xi$$

solves the equation with $\epsilon = \frac{3}{2}$. This gives an eigenfunction of the form



which would then correspond to the second energy level.

We now see that there is an algorithm for finding polynomial solutions to this differential equation. Look for a solution of the form

$$h_n(\xi) = \xi^n + \dots$$

plus lower-order polynomial terms. Plugging this into the equation, we find

$$\mathcal{O}(\xi^{n-2}) - 2n\xi^n + (2\epsilon-1)\xi^n + \mathcal{O}(\xi^{n-4}) = 0$$

This is consistent if

$$\epsilon = n + \frac{1}{2}$$

The next terms are proportional to ξ^{n-2} . We can solve for the coefficient of the ξ^{n-2} term in $h(\xi)$ in terms of the coefficient of the ξ^n term. The equation never generates terms with negative powers of ξ , only lower-order polynomials, so the process eventually ends with the ξ^1 or ξ^0 term. Proceeding in this way, we find for every n a solution of the form

$$h_n(\xi) = \xi^n + a\xi^{n-2} + b\xi^{n-4} + \dots$$

where the coefficients a , b , etc. are determined. The next solution beyond the ones given above is

$$h_2(\xi) = \xi^2 - \frac{1}{2}$$

The differential equation

$$H'' - 2\xi H' + 2n H = 0$$

was actually studied by Hermite in the 19th century. The polynomial solutions that I have discussed are called the *Hermite polynomials*. Conventionally, the Hermite polynomials are normalized so that the leading term is

$$H_n(\xi) = 2^n \xi^n + \dots$$

The Hermite polynomials have an interesting mathematical theory. These polynomials can be expressed as the successive terms in the expansion of a *generating function* $S(\xi, s)$

$$S(\xi, s) = e^{\xi^2} e^{-(\xi-s)^2} = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(\xi)$$

The function $S(\xi, s)$ satisfies the equation

$$\frac{\partial^2}{\partial \xi^2} S - 2\xi \frac{\partial}{\partial \xi} S + 2s \frac{\partial}{\partial s} S = 0$$

If we expand this order by order in s , we find the Hermite equation for each n . This approach gives the following alternative expression for the Hermite polynomials:

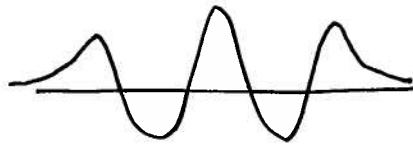
$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

for $n = 0, 1, 2, \dots$

We have now found an infinite discrete family of eigenfunctions of the quantum harmonic oscillator problem

$$\psi_n(x) = N_n H_n(\xi) e^{-\frac{1}{2}\xi^2} \quad \xi = \left(\frac{m\Omega}{\hbar}\right)^{\frac{1}{4}} x$$

for $n = 0, 1, 2, \dots$, where N_n is a constant that normalizes the wavefunction. The n th wavefunction has the shape



with n zeros. This is just the shape we expect for the $(n + 1)$ st energy eigenfunction. These functions then account for the full set of discrete eigenfunctions of this problem.

These wavefunctions are normalized if

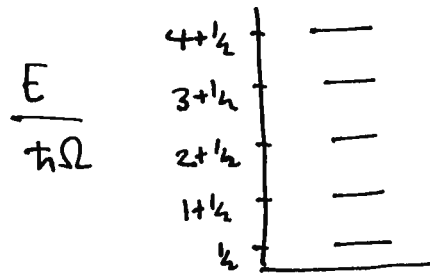
$$N_n = \left(\frac{1}{\sqrt{\pi} 2^n n!}\right)^{\frac{1}{2}} \left(\frac{m\Omega}{\hbar}\right)^{\frac{1}{4}}$$

This relation can be proved using generating function.

The formula for the energy levels is very simple:

$$E_n = \hbar \Omega \left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, \dots$$

The levels form a pattern with equal spacing



In the study of atoms or other quantum systems, a set of levels with equal spacing indicates that the system contains component that is well approximated by a harmonic oscillator.

Once we have constructed the full set of eigenvectors, we can solve the initial value problem for the Schrödinger equation in the same way that we solved the initial value problem for the square well. Start with an initial condition $\psi_0(x)$, which should be a smooth function with correct boundary conditions as $|x| \rightarrow \infty$. I claim that any such function can be approximated as a linear combination of the eigenstates

$$\psi_0(x) = \sum_{n=0}^{\infty} c_n \psi_n(x) = \sum_{n=0}^{\infty} c_n N_n H_n(\xi) e^{-\frac{1}{2}\xi^2}$$

where, again

$$\xi = \left(\frac{m\Omega}{\hbar}\right)^{\frac{1}{2}} x$$

I will not prove the claim here, but I hope you find it reasonable. An appropriate $\psi_0(x)$ has the form

$$\psi_0(x) = \mathcal{P}(\xi) e^{-\frac{1}{2}\xi^2}$$

Over any finite interval, the function $\mathcal{P}(\xi)$ can be approximated by a polynomial. If we choose the interval $(-b, b)$ such that

$$e^{-\frac{1}{2}b^2} = 10^{-20} \quad b = 9.4$$

we obtain a very accurate approximation. The polynomial can then be written as a linear combination of Hermite polynomials. Once we have obtained $\psi_0(x)$ in the above form, we can solve the Schrödinger equation by giving each term its appropriate time-dependence. Then the solution is

$$\begin{aligned} \Psi(x,t) &= \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-i E_n \frac{1}{\hbar} t} \\ &= e^{-i \Omega t / 2} \left[\sum_{n=0}^{\infty} c_n \psi_n(x) e^{-i n \Omega t} \right] \end{aligned}$$

Notice that this general solution of the time-dependent Schrödinger equation is (up to the pure phase in front) periodic with period

$$T = \frac{2\pi}{\Omega}$$

The probability density

$$P(x,t) = |\Psi(x,t)|^2$$

is periodic with this same period T . Thus, the quantum harmonic oscillator really does predict periodic oscillations with the expected frequency Ω .

To complete this argument, I would like to give a better method for finding the approximation coefficients c_n . The proof of the orthogonality of wavefunctions of different energy applies here using the same arguments that I gave in discussing the square well potential. Then, here also,

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) dx = \delta_{mn} = \begin{cases} 1 & m=n \\ 0 & m \neq n \end{cases}$$

The eigenfunctions are orthogonal and, with the coefficient given above, also normalized. Then the c_n are given by the integral

$$c_n = \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi_0(x)$$

I would like to say one more thing about the orthogonality of these eigenfunctions. The orthogonality relation, written explicitly, is

$$\int_{-\infty}^{\infty} dx (H_n(\xi) e^{-\frac{1}{2}\xi^2}) (H_m(\xi) e^{-\frac{1}{2}\xi^2}) = 0$$

for $n \neq m$

or

$$\int_{-\infty}^{\infty} d\xi e^{-\xi^2} H_n(\xi) H_m(\xi) = 0$$

This equation can be rewritten in an interesting way. Define a measure

$$\int d\mu = \int_{-\infty}^{\infty} d\xi e^{-\xi^2}$$

Then the orthogonality relation takes the simpler or more obvious form

$$\int d\mu H_n^*(\xi) H_m(\xi) = 0 \quad \text{if } m \neq n$$

We say: If $n \neq m$, the Hermite polynomials $H_m(\xi)$, $H_n(\xi)$ are orthogonal under the measure μ .

We already know that this equation is true, but anyway I would like to give a direct proof. Start from the Hermite equation

$$\left(-\frac{d^2}{d\xi^2} + 2\xi \frac{d}{d\xi}\right) H_n(\xi) = 2n H_n(\xi)$$

This allows us to write

$$\int d\mu \left\{ H_n^*(\xi) \left(-\frac{d^2}{d\xi^2} + 2\xi \frac{d}{d\xi}\right) H_m(\xi) \right\} = 2m \int d\mu H_n^* H_m$$

$$\int d\mu \left\{ \left(-\frac{d^2}{d\xi^2} + 2\xi \frac{d}{d\xi}\right) H_n^*(\xi) \cdot H_m(\xi) \right\} = 2n \int d\mu H_n^* H_m$$

We can prove orthogonality if we can show that the left-hand sides of these two equations are equal. To do this, integrate by parts. All boundary terms at $\pm\infty$ vanish. Then

$$\begin{aligned} \int d\mu \left(2\xi \frac{d}{d\xi} H_n^*(\xi) \right) (H_m(\xi)) &= \int_{-\infty}^{\infty} d\xi \left(\frac{d}{d\xi} H_n^* \right) (2\xi e^{-\xi^2} H_m(\xi)) \\ &= \int_{-\infty}^{\infty} d\xi H_n^* \cdot \left\{ (-2e^{-\xi^2} + 4\xi^2 e^{-\xi^2} - 2\xi e^{-\xi^2} \frac{d}{d\xi}) H_m \right\} \end{aligned}$$

and

$$\begin{aligned} \int d\mu \left(-\frac{d^2}{d\xi^2} H_n^* \right) H_m &= \int_{-\infty}^{\infty} d\xi \left(-\frac{d^2}{d\xi^2} H_n^* \right) (e^{-\xi^2} H_m) \\ &= \int_{-\infty}^{\infty} d\xi \left(\frac{d}{d\xi} H_n^* \right) \left\{ (-2\xi e^{-\xi^2} + e^{-\xi^2} \frac{d}{d\xi}) H_m \right\} \\ &= \int_{-\infty}^{\infty} d\xi H_n^* \left\{ (2e^{-\xi^2} - 4\xi^2 e^{-\xi^2} + 2\xi e^{-\xi^2} \frac{d}{d\xi} \right. \\ &\quad \left. + 2\xi e^{-\xi^2} \frac{d}{d\xi} - e^{-\xi^2} \frac{d^2}{d\xi^2}) H_m \right\} \end{aligned}$$

Summing the pieces, we find

$$\int d\mu H_n^* \left\{ (-2 + 4\xi^2 - 2\xi \frac{d}{d\xi} + 2 - 4\xi^2 + 4\xi \frac{d}{d\xi} - \frac{d^2}{d\xi^2}) H_m \right\}$$

or, finally,

$$\int d\mu \left[\left(-\frac{d^2}{d\xi^2} + 2\xi \frac{d}{d\xi} \right) H_n^* \right] H_m = \int d\mu H_n^* \left(-\frac{d^2}{d\xi^2} + 2\xi \frac{d}{d\xi} \right) H_m$$

So, the method works. We find

$$2_m \left(\int d\mu H_n^* H_m \right) = 2_n \left(\int d\mu H_n^* H_m \right)$$

Then Hermite polynomials with different index n are orthogonal under the measure μ . This gives another piece of the theory that we are progressively developing.