

## 4.2: Solving the Schrödinger Equation

It is convenient to make the substitution that

$$x = (z_2 - z_1 - r_e)$$

This allows us to write the Hamiltonian for the system then as

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where  $\mu$  is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$k$  is the force constant of the bond and  $x$  is defined by

$$x = (r - r_e)$$

as previously state. The Schrödinger equation is then given by

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2\right) \psi(x) = E\psi(x)$$

### Energy Levels

The boundary conditions require that the square of the wavefunction must have a finite area below it in order to ensure that the wavefunction is normalizable. The only way this happens is if the following conditions are met

$$\lim_{x \rightarrow \pm\infty} \psi(x) = 0$$

The resulting energy levels are the set of eigenvalues that correspond to the functions that satisfy the above stated boundary condition. These energies have values given by

$$E_v = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2}\right) \quad v = 0, 1, 2, 3, \dots$$

Notice how the use of the boundary conditions is what leads to the instruction of quantized energies.

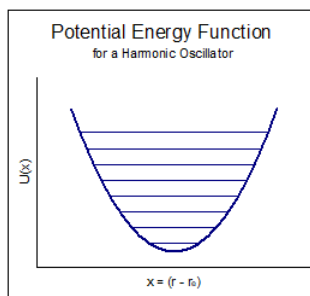


Figure 4.2.2

The resulting energy levels are evenly spaced with increasing energy. The actual spacing is determined by the physical characteristics of a given molecule, namely the reduced mass and the force constant.

### Spectroscopic Constants and Force Constants

Vibrational spectroscopy is often done using units of  $cm^{-1}$ . Energies expressed in terms of this unit are called **term values**. The termvalue is given as the energy divided by Planck's constant and the speed of light ( $E/hc$ ). Standard notation uses the symbol  $G_v$  to indicate the term value for vibrational energy.  $G_v$  is given by

$$G_v = \frac{E_v}{hc} = \omega_e \left(v + \frac{1}{2}\right)$$

where

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

The vibrational constant  $w_e$  can be determined experimentally for specific molecules. Consider the following values for various molecules.

Molecule	$\omega_e (cm^{-1})$	k (N/m)	$\mu$ (kg)
$^1H^{35}Cl$	2989.74	516	$1.627 \times 10^{-27}$
$^1H^{79}Br$	2649.67	412	$1.652 \times 10^{-27}$
$^1H^{127}I$	2309.5	314	$1.660 \times 10^{-27}$
$^{19}F^{19}F$	916.64	347	$1.577 \times 10^{-26}$
$^{16}O^{16}O$	1580.93	1177	$1.328 \times 10^{-26}$
$^{14}N^{14}N$	2359.61	3116	$1.163 \times 10^{-26}$

Two important points can be made from this data. First, a typical force constant for a single bond is on the order of a couple hundred N/m. Secondly, multiple bonds lead to significantly larger force constants. This is not too surprising since the force constant gives a measure of the stiffness of the bond.

## The Wavefunctions

The wavefunctions for the harmonic oscillator are determined by solving the Schrödinger equation. As stated before, the only wavefunctions that obey the boundary conditions have eigenvalues given by

$$E_v = \hbar \sqrt{\frac{k}{\mu}} (v + 1/2)$$

where  $v = 0, 1, 2, 3, \dots$ . The wavefunctions themselves can be determined by solving the differential equation using a power-series solution. In the end, we find that the resulting function involve a set of **orthogonal polynomials** known as the **Hermite Polynomials**. We will discuss some properties of this important set of functions before discussing the wave functions themselves.

## Hermite Polynomials

The **Hermite polynomials** are a set of orthogonal polynomials. Like all sets of orthogonal polynomials, they have 1) a generator formula, 2) an orthogonality relationship and 3) a (or several) recursion relations that relate one function in the series to others.

The Hermite polynomials can be generated using the following function

$$H_v(y) = (-1)^v e^{y^2} \frac{d^v}{dy^v} e^{-y^2}$$

Using this function, the first few Hermite polynomials can be generated.

v	$H_v(y)$
0	1
1	2y
2	$4y^2 - 2$

Further members of the set of functions can be generated using one of the important recursion relations.

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

Using this function, we can generate a longer list of Hermite polynomials without having to take so many derivatives.

$v$	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
	<i>Etc.</i>

Another important relationship between these functions is that

$$\frac{d}{dy} H_v(y) = 2v H_{v-1}(y)$$

In addition to these relationships, the Hermite polynomials have an important orthogonality relationship.

$$\int_{-\infty}^{\infty} H_v(y) H_{v'}(y) e^{-y^2} dy = v! 2^v \sqrt{\pi} \delta_{vv'}$$

The Hermite polynomials also have important symmetry properties. Each function in the set is an eigenfunction of the **inversion operator**. The inversion operator is a symmetry operator that is defined by the operation (in one dimension)

$$\hat{i} f(x) = f(-x)$$

Functions that are eigenfunctions of this operator can be classified as being either **even function** or **odd function**.

Even	$f(-x) = f(x)$
Odd	$f(-x) = -f(x)$

Even functions are **symmetric** eigenfunctions of the inversion operator and odd functions are **antisymmetric** eigenfunctions as their eigenvalues are +1 and -1 respectively. Even and odd functions also have important properties when integrated over symmetric intervals.

Even	$\int_{-a}^a f(x) dx = 2 \int_0^a f(x) dx$
Odd	$\int_{-a}^a f(x) dx = 0$

These properties can greatly simplify integration involving these types of functions!

### The Harmonic Oscillator Wavefunctions

The wavefunctions for the Harmonic Oscillator have three important parts: 1) a normalization constant, 2) a Hermite polynomial and 3) an exponential function that insures the orthogonality of the wavefunctions.

$$\psi_v(x) = N_v H_v \left( \alpha \frac{1}{2} x \right) e^{-\alpha x^2/2}$$

where

$$\alpha = \sqrt{k \cdot \mu} \text{ and } N_v = \sqrt{\frac{\sqrt{\alpha/\pi}}{2^v \cdot v!}}$$

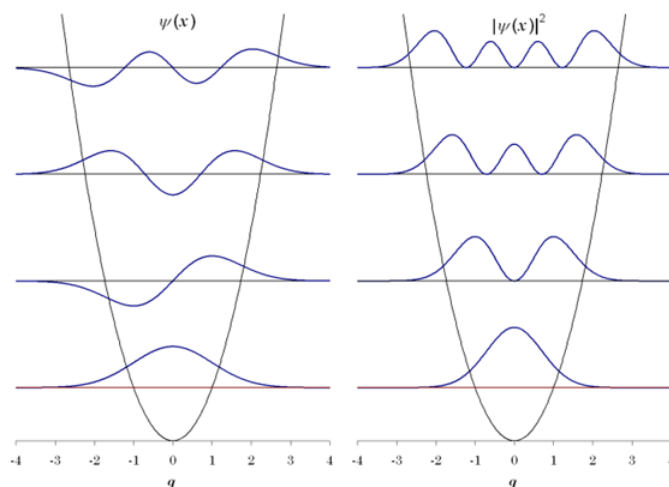


Figure 4.2.3

## Expectation Values

The simplicity of the wavefunctions makes the calculation of expectation values very simple for the harmonic oscillator problem.

### Position

The expectation value of position can be determined solely based on symmetry arguments. Recall that harmonic oscillator wavefunctions are either even or odd functions. The symmetry of the products of even or odd functions can be summarized as follows.

	even	odd
even	even	odd
odd	odd	even

It is easy to recognize this multiplication table as arising from taking the products of the eigenvalues of the functions with respect to the inversion operator.

	1	-1
1	1	-1
-1	-1	1

These results will be used to demonstrate that the expectation value of position is the same for all of the stationary wavefunction. Consider the integral required to calculate this value.

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v \cdot x \cdot \psi_v dx$$

The wavefunction  $\psi_v$  is either an even or odd function depending only on whether v is even or odd. Since the  $\hat{x}$  operator is itself an odd function (always), there are only two possibilities for the total symmetry of the integrand.

$\psi_v$	$x$	$\psi_v$	Integrand Symmetry
even	odd	even	odd
odd	odd	odd	odd

The pattern emerges due to the fact that the product of even and odd function produces a resulting function according to the following symmetry multiplication table.

Regardless of whether the wavefunction is an even or odd function, the product

$$\psi_v \cdot x \cdot \psi_v$$

is always an odd function. And as we have seen before, the integral of an odd function over any symmetric interval is zero by symmetry.

Therefore, the expectation value of  $x$ ,  $\langle x \rangle$ , is always 0 for any eigenstate of the harmonic oscillator. This means that  $\langle r \rangle = r_e$ , the equilibrium bond length.

## Momentum

The evaluation of the expectation value of momentum can be made following the same symmetry arguments. In order to do this, one must consider the effect of taking a derivative of a function.

Consider the following even function

$$f(x) = 4x^2 - 2$$

The first derivative of this function is given by

$$\frac{d}{dx} f(x) = 8x$$

which is an odd function. The derivative of this function

$$\frac{d}{dx} 8x = 8$$

yields an even function. The following set of properties will hold for the symmetries of functions and their derivatives.

$f(x)$	$\frac{d}{dx} f(x)$
even	odd
odd	even

As such, the symmetry of the integrand for the calculation of the expectation value of momentum

$$\int_{-\infty}^{\infty} \psi_v \hat{p} \psi_v dx$$

must always be an odd function, since the  $\hat{p}$  takes the first derivative of the wavefunction.

$\psi_v$	$\hat{p} \cdot \psi_v$	Integrand Symmetry
even	odd	odd
odd	even	odd

The result is that the expectation value of momentum,  $\langle p \rangle$ , must also be 0 for any eigenstate of the harmonic oscillator problem. Again, this can be reasoned by noting that half of the time the momentum measured will be in the direction of the bond stretching, and the other half of the time in the direction of the bond being compressed. On average, these two circumstances will cancel, yielding an average value of  $\langle p \rangle = 0$ .

## Energy

As with any eigenstate, the expectation value of energy  $\langle E \rangle$  is easy to calculate. Recall that the wavefunctions were determined to be eigenfunctions of the Hamiltonian.

$$\hat{H}\psi_v = E_v\psi_v$$

As such, The expectation value of energy is trivially easy to find for a system in an eigenstate.

$$\begin{aligned}
 \langle E \rangle &= \int_{-\infty}^{\infty} \psi_v \hat{H} \psi_v dx \\
 &= \int_{-\infty}^{\infty} \psi_v E_v \psi_v dx \\
 &= E_v \int_{-\infty}^{\infty} \psi_v \psi_v dx \\
 &= E_v
 \end{aligned}$$

since the wavefunctions are normalized. The expectation value of energy is always an eigenvalue of the Hamiltonian for a system that is in an eigenstate of the Hamiltonian.

## Tunneling

One of the curious consequences of quantum mechanics can be seen in the form of **tunneling**. This odd behavior becomes possible whenever the square of the wavefunction extends beyond a classical barrier to the motion of the particle or molecule. In the case of the harmonic oscillator, this is seen as possible since the squared wavefunction extends beyond the classical turning points of the oscillation.

The classical turning point is defined as the point in the motion where all energy has been converted from kinetic energy to potential energy. At this point, the motion switches direction as potential energy is converted back into kinetic energy. Since there is a non-zero value of the squared wavefunction beyond this point for all eigenstates, there is a non-zero probability of measuring the position of the system to lie beyond these classical turning points. And then if there is a new potential well accessible if the system tunnels through the classical barrier, there is a non-zero probability of finding the system in that well, meaning that the system may have changed states completely!

This result is another example of the bizarreness of quantum mechanics. If one were to consider a classical ball that is thrown against the wall at the front of the classroom, one expects that the ball will return to the thrower after bouncing off the wall every time. But for a quantum mechanical ball, there is a non-zero possibility of finding the ball on the other side of the wall! If this were to be the case, the ball would have been said to have tunneled through the wall.

The probability for this happening is proportional to that fraction of the area under the squared wavefunction curve that lies beyond the classical barrier. This probability will be decreased for heavier objects as the fraction of wavefunction beyond the classical barrier will be smaller.

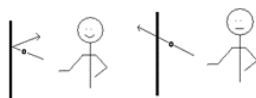


Figure 4.2.4

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