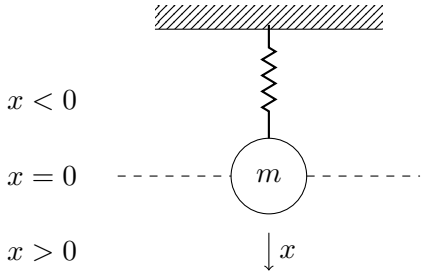
CHM 305 - Lecture 10 - The Harmonic Oscillator

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Today we will briefly discuss the classical harmonic oscillator, and then lead into the quantum harmonic oscillator and its eigenfunction and eigenvalue solutions. We will draw a connection to treating the vibrations of molecular bonds. The material in today's lecture is covered in much more detail in Chapter 5 of McQuarrie.

1 The Classical Harmonic Oscillator

Let's review the classical harmonic oscillator. We consider a mass on a spring dangling from a rigid ceiling; we can show that this system has sinusoidal displacement in time.



In the absence of any perturbations, the mass hangs at its equilibrium position $x = 0$. If we compress or extend the spring, we subject the system to a displacement from equilibrium. For an extension of the spring, $x > 0$, for a compression, $x < 0$.

We know intuitively that a spring applies a force that opposes our effort in either direction. Mathematically, this is expressed by Hooke's law:

$$F = -kx \tag{1}$$

Here k is the force constant with units of N/m. This constant describes the stiffness of the spring.

Imagine that we grab the mass m and pull it downward towards $x > 0$, and then release it. We expect to see oscillatory behavior. In the absence of energy dissipation or friction, this oscillation will continue indefinitely. We want to find a mathematical expression for the extension of the spring as a function of time, $x(t)$. Let's begin with Newton's second law:

$$F = ma = m\ddot{x} = m\frac{d^2x}{dt^2} \tag{2}$$

We also have an expression for force from Hooke's law (Eqn. 1), so putting the two together we

can arrive at a simple differential equation:

$$F = m\frac{d^2x}{dt^2} = -kx \tag{3}$$

$$\rightarrow m\frac{d^2x}{dt^2} + kx = 0 \tag{4}$$

We can solve this differential expression to obtain a form for $x(t)$. Since we're looking for functions proportional to their own second derivatives, sine and cosine functions should do the trick. So let's make a guess for $x(t)$:

$$x(t) = A\sin(\omega t) + B\cos(\omega t) \tag{5}$$

We find the oscillation frequency ω by plugging Eqn. 5 back into the differential equation in Eqn. 4. In order for $x(t)$ to satisfy the differential equation for all times t, we must have:

$$\boxed{\omega = \sqrt{\frac{k}{m}}} \tag{6}$$

ω is the angular frequency of oscillation (units of radians/second), which we can now describe in terms of the physical constraints of the system.

Note that ω is completely determined by k and m and any perturbation will cause the mass to oscillate at frequency ω and no other. We would have to change the mass m or spring constant k in order to change ω.

We can plug our expression for ω into Eqn. 5 and write down a more complete expression for $x(t)$:

$$x(t) = A\sin(\omega t) + B\cos(\omega t) = A\sin\left(\sqrt{\frac{k}{m}}t\right) + B\cos\left(\sqrt{\frac{k}{m}}t\right) \tag{7}$$

Note that the coefficients A and B have not yet been determined. A and B together will constrain the amplitude and phase of the oscillation, and are specified by the initial conditions, e.g. the position and velocity of the mass at $t = 0$.

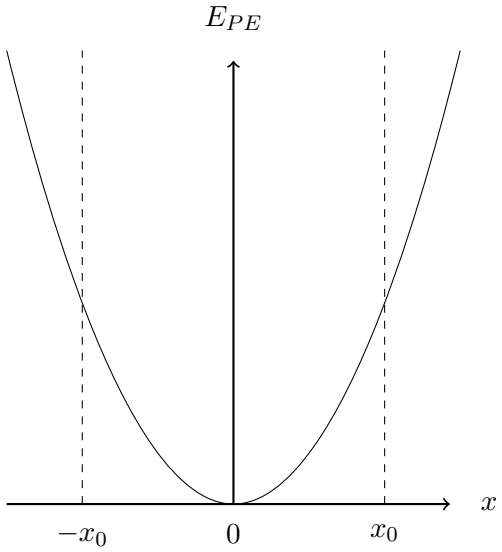
One more useful thing to note about the classical harmonic oscillator is its potential energy landscape. We know from classical Newtonian mechanics that potential energy is the integral of the applied force over some distance. So we can write the potential energy of pushing the mass from position $x = 0$ to some value x_0 as:

$$E_{PE} \equiv V(x_0) = \int_0^{x_0} F \cdot dx = \int_0^{x_0} kx \cdot dx = \left[\frac{1}{2}kx^2\right]_0^{x_0} = \frac{1}{2}kx_0^2 \tag{8}$$

The potential energy of a harmonic oscillator is therefore *quadratic in the displacement from equilibrium.*

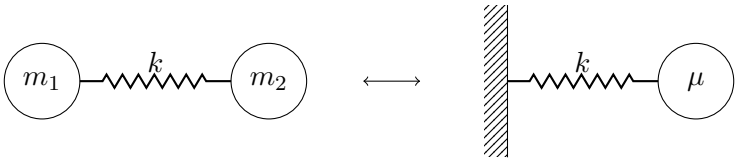
We can also conceive of the harmonic oscillator problem as a ball rolling back and forth in a frictionless parabolic well. It reaches the *classical turning points* of its trajectory, $\pm x_0$ in the figure below, at the positions where all of the ball's initial kinetic energy has been converted into potential energy.

In the quantum harmonic oscillator system, we will consider solutions to the Schrödinger equation for a particle exploring this potential, $V(x) = \frac{1}{2}kx^2$. We will find that the quantum harmonic oscillator wavefunctions extend beyond the classical turning points, and tunnel slightly into the parabolic walls of the potential. Our solutions will look similar to those of the finite square well, but their forms will be more complicated because the walls of the potential are curved.



2 The Quantum Harmonic Oscillator

Let's start by considering two masses m_1 and m_2 connected by a spring. We can imagine that this system might be a reasonable model for the vibration of a diatomic molecule held together by a chemical bond, which like a mechanical spring has an equilibrium position and resists being compressed or extended. In a molecule, we have very small masses, separated by a very small distance, and so this size scale demands that we think about this problem within the context of quantum mechanics.

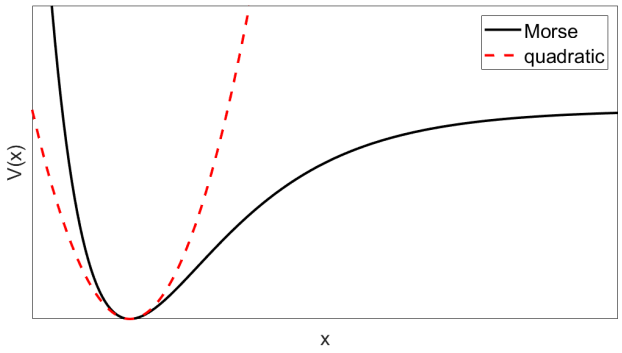


Because the vibration of this system involves the motion of two masses, we have to be a little careful. We can reduce the movement of these two connected bodies to a one-body problem concerning the motion of an effective mass relative to a fixed rigid wall. To do so, we use the ***reduced mass***:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{9}$$

As we just learned for the classical harmonic oscillator, if the spring provides a linear restoring force $F = -kx$, the potential energy for this system will be a quadratic function of x with $V(x) = \frac{1}{2}kx^2$, where the equilibrium position is $x = 0$ at the minimum of the potential well where $V(0) = 0$.

Is this harmonic potential a good approximation for the vibrational motion of the two atoms in a diatomic molecule? The actual internuclear potential for a diatomic molecule is more like the Morse potential plotted below. This more accurate potential rises steeply at short bond lengths as you push the nuclei closer together, due to the repulsion of overlapping electron orbitals at short ranges. At large bond lengths, the potential rises gradually and levels off as the atoms are far apart and no longer interact.



The dashed line shows the harmonic oscillator potential. While it may first appear to be a terrible model for a diatomic molecule, it actually matches the Morse potential quite well in the region near the minimum. This region is the most physically important region for most molecules ***as long as they are near equilibrium***. The harmonic oscillator model is therefore a reasonably good approximation as long as we are only considering small displacements in the bond length x.

3 Solutions to the Quantum HO Schrödinger Equation

Let's write down the time-independent Schrödinger equation for the vibrations of this molecule, which we would solve to find the wavefunctions and allowed energies for our system.

$$\hat{H}\psi_n(x) = -\frac{\hbar^2}{2\mu}\frac{d^2}{x^2}\psi_n(x) + \frac{1}{2}kx^2\psi_n(x) = E_n\psi_n(x) \tag{10}$$

$$\rightarrow \frac{d^2\psi_n(x)}{dx^2} = \frac{2\mu}{\hbar^2}\left(\frac{1}{2}kx^2 - E_n\right)\psi_n(x) \tag{11}$$

Note that we use the reduced mass μ here instead of the mass of either atom.

The solution of this differential equation is considerably more involved than the ones we have considered so far. The second derivative of $\psi(x)$ is now proportional to itself times a polynomial in x! The solutions are not going to be simple sinusoidal or exponential functions like we saw for the free particle or particles in boxes.

We won't go through the math here to derive solutions to this differential equation. Instead, I will give you the solutions for the wavefunctions, and we'll show that at least the lowest-energy wavefunction indeed solves the Schrödinger equation. In your problem set you'll check that a higher energy solution solves the Schrödinger equation as well.

The wavefunctions for the quantum harmonic oscillator take the form of a polynomial in x denoted $H_n(x)$ multiplied by an Gaussian exponential decay:

$$\psi_n(x) = N_n\, H_n(\alpha^{1/2}x)\, e^{-\alpha x^2/2}, \qquad n = 0, 1, 2, \ldots \tag{12}$$

where

$$\alpha \equiv \sqrt{\frac{k\mu}{\hbar^2}} \tag{13}$$

and the normalization constant for each wavefunction is

$$N_n = \frac{1}{(2^n\, n!)^{1/2}} \left(\frac{\alpha}{\pi}\right)^{1/4} \tag{14}$$

and $H_n(\alpha^{1/2}x)$ are a special set of polynomials called Hermite polynomials, expressed as functions of $\alpha^{1/2}x$. The first few Hermite polynomials are:

$$H_0(y) = 1 \tag{15}$$

$$H_1(y) = 2y \tag{16}$$

$$H_2(y) = 4y^2 - 2 \tag{17}$$

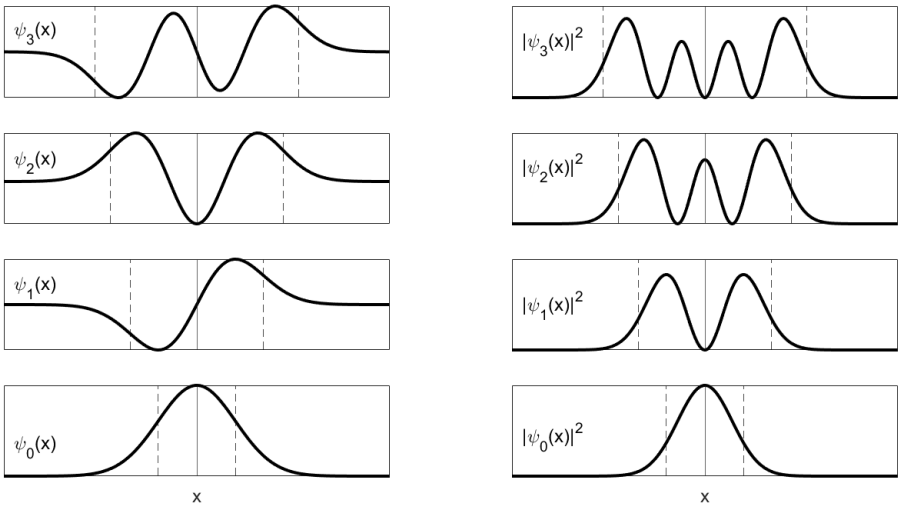
$$H_3(y) = 8y^3 - 12y \tag{18}$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \tag{19}$$

$$\ldots$$

There is no closed form expression for the Hermite polynomials; but the $(n+1)^{\text{th}}$ polynomial can be generated iteratively from the n^{th}. McQuarrie Chapter 5 has much more detail on this for those interested.

Let's plot these first few wavefunctions and their square norms. The n^{th} wavefunction has n nodes. Looking a little bit ahead, as we will consider the energies of these wavefunctions, I am also plotting with dashed vertical lines the positions of the classical turning points in the potential energy surface. It's clear that the quantum particle will tunnel past these classical turning points with a decaying probability given by its Gaussian envelope.



Let's consider the eigenfunction with quantum number $n = 0$, show that this expression solves the Schrödinger equation, and find the energy eigenvalue E_0.

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \tag{20}$$

$$\hat{H}\psi_0 = -\frac{\hbar^2}{2\mu}\frac{d^2\psi_0}{dx^2} + \frac{kx^2}{2}\psi_0 \stackrel{?}{=} E_0\,\psi_0 \tag{21}$$

$$= -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\left(c\cdot e^{-\alpha x^2/2}\right) + \frac{kx^2}{2}\left(c\cdot e^{-\alpha x^2/2}\right) \tag{22}$$

$$= -\frac{\hbar^2}{2\mu}\frac{d}{dx}\left(c\cdot(-\alpha x)\cdot e^{-\alpha x^2/2}\right) + \frac{kx^2}{2}\left(c\cdot e^{-\alpha x^2/2}\right) \tag{23}$$

$$= -\frac{\hbar^2}{2\mu}\left(-c\cdot\alpha\cdot e^{-\alpha x^2/2} + c\cdot(\alpha x)^2\cdot e^{-\alpha x^2/2}\right) + \frac{kx^2}{2}\left(c\cdot e^{-\alpha x^2/2}\right) \tag{24}$$

$$= \left(c\cdot e^{-\alpha x^2/2}\right)\left(\frac{\hbar^2\alpha}{2\mu} - \cancel{\frac{\hbar^2\alpha^2}{2\mu}}x^2 + \cancel{\frac{k}{2}}x^2\right) = \psi_0(x)\cdot\frac{\hbar^2\alpha}{2\mu} \equiv \psi_0(x)\cdot E_0 \tag{25}$$

where in the last line we have used the fact that $\alpha^2 = \frac{k\mu}{\hbar^2}$. Therefore, we have:

$$\rightarrow E_0 = \frac{\hbar^2\alpha}{2\mu} = \frac{\hbar^2}{2\mu}\cdot\left(\frac{k\mu}{\hbar^2}\right)^{1/2} = \frac{\hbar}{2}\left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2}\hbar\omega \tag{26}$$

where we have defined $\omega \equiv \sqrt{\frac{k}{\mu}}$, just the same as it was for the classical harmonic oscillator.

If we repeat this process for higher-energy eigenstates, it will turn out that the general form of the energy eigenvalues for the quantum harmonic oscillator are

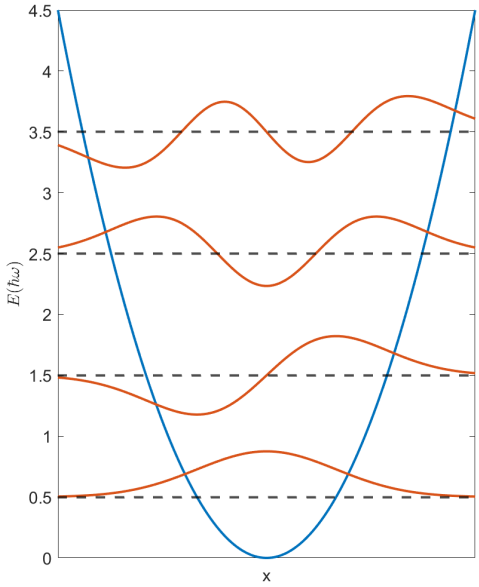
$$E_n = \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(n+\frac{1}{2}\right) \quad = \quad \hbar\omega\left(n+\frac{1}{2}\right) \quad = \quad h\nu\left(n+\frac{1}{2}\right) \tag{27}$$

where

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \text{and} \qquad \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{28}$$

These energy eigenvalues are therefore evenly spaced with separation $\Delta E = \hbar\omega = h\nu$ between neighboring rungs. ***The uniform spacing of these discrete energy states is unique to the quantum harmonic oscillator.*** This is very special: the potential has *just* the right shape to give rise to uniformly spaced energy levels.

Let's plot our wavefunctions again, this time superimposed on top of an energy diagram inside the quadratic potential. The $V(x)$ potential crosses the energy eigenvalues where the classical turning points would be. Just as we saw for the particle in a finite box, the wavefunctions tunnel into the walls of the potential with a decaying tail, this time with a Gaussian dependence $\propto e^{-\alpha x^2/2}$.



Note also that the $n = 0$ state has non-zero energy $E_0 = \frac{1}{2}\hbar\omega$, which is another instance of "zero point energy" like we saw for the particle in a box. A particle in a harmonic oscillator potential can never have lower energy than $\frac{1}{2}\hbar\omega$.

What is the reason for this zero point energy? Now that we have learned about the uncertainty principle we can motivate this phenomenon more clearly.

The Hamiltonian for the quantum harmonic oscillator consists of the usual kinetic energy and potential energy components and can be written as:

$$\hat{H}\psi(x) = \left[\underbrace{\frac{\hat{p}^2}{2\mu}}_{\text{KE}} + \underbrace{\frac{k\hat{x}^2}{2}}_{\text{PE}}\right]\psi(x) = E\psi(x) \tag{29}$$

If we claim that it is possible for a quantum particle to have $E = 0$, then both KE and PE would have to go to zero, and accordingly $\hat{p}^2$ and $\hat{x}^2$ would both have to be exactly 0.

We learned from the uncertainty principle that $\hat{p}$ and $\hat{x}$ do not commute and thus we cannot know their values simultaneously. To set their squares both exactly to 0 would therefore violate the uncertainty principle. Accordingly, the energy of the system cannot be 0, and hence the system has zero point energy.

4 Some Nice Properties of Harmonic Oscillator Wavefunctions

Let's consider some properties of our harmonic oscillator eigenfunctions. They have complex forms, and therefore it can be tedious to use them to perform integrals to calculate probabilities and expectation values. But we can use a nice trick to avoid many annoying integrals: symmetry.

In particular, it is helpful to think about whether each wavefunction is *even* or *odd*. An even function is symmetric when reflected across the y axis, and an odd function changes sign.

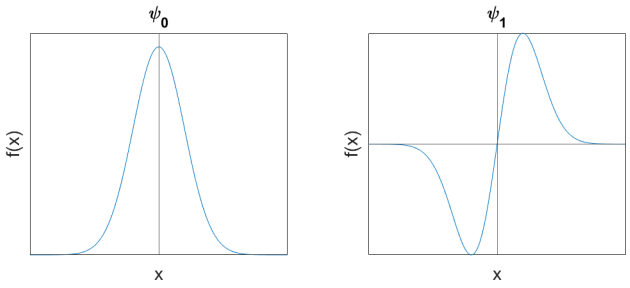
$$f(x) = f(-x) \qquad \text{for } f(x) \text{ even} \tag{30}$$

$$f(x) = -f(-x) \qquad \text{for } f(x) \text{ odd} \tag{31}$$

From these definitions we can write out a few rules for how these functions behave:

- odd $\times$ odd = even
- even $\times$ even = even
- odd $\times$ even = odd
- the derivative of an odd function is even
- the derivative of an even function is odd

It turns out that all quantum HO wavefunctions $\psi_n(x)$ with even n are even, and those with odd n are odd. Additionally, the square of both even and odd functions is always even, so $|\psi_n(x)|^2$ is even for all quantum numbers n.



This even-odd property is quite special and allows us to drastically simplify many integrals. For instance, the integral of an odd function is always 0 when evaluated symmetrically about $x = 0$:

$$\int_{-A}^{A} f(x)dx = 0 \qquad \text{if } f(x) \text{ is odd} \tag{32}$$

We can make use of this property to find the expected values $\langle x \rangle$ and $\langle p \rangle$ for the quantum harmonic oscillator wavefunctions $\psi_n(x)$.

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, \hat{x}\, \psi_n(x)dx = \int_{-\infty}^{\infty} x\, |\psi_n(x)|^2 dx = 0 \tag{33}$$

The product of an odd function, x, and an even function $|\psi_n(x)|^2$ is always odd, so the integrand here is an odd function of x, and the integral is therefore 0, and $\langle x \rangle = 0$. Thus, the average

displacement of a quantum harmonic oscillator is zero for all quantum states, meaning the average internuclear separation of our diatomic molecule is the equilibrium position, $x = 0$, as expected.

Finding $\langle p \rangle$ is a similar proposition:

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, \hat{p}\, \psi_n(x)\, dx = \int_{-\infty}^{\infty} \psi_n^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi_n(x)\, dx \tag{34}$$

$$= -i\hbar \int_{-\infty}^{\infty} \psi_n^* \cdot \frac{d\psi_n}{dx} dx = 0 \tag{35}$$

The first derivative of an odd function is always even, and that of an even function is always odd. So the product of $\psi_n(x)$ and its derivative is always the product of one even and one odd function. Therefore this integrand is always odd, and its integral over all x vanishes. We therefore conclude that the average momentum of any eigenfunction of this system: $\langle p \rangle = 0$.

5 The Harmonic Oscillator and Vibrational Spectroscopy

The infrared spectrum of a diatomic molecule can be modeled by treating its vibrational levels as a quantum harmonic oscillator and considering transitions between these levels. We have just learned that the energy levels of the quantum harmonic oscillator are given by:

$$E_n = h\nu \left(n + \frac{1}{2} \right) = \hbar\omega \left(n + \frac{1}{2} \right) \qquad n = 0, 1, 2, \ldots \tag{36}$$

where $\omega = \sqrt{\frac{k}{\mu}}$.

The molecule can make a transition from one vibrational energy level (n) to another (n') by absorbing or emitting radiation whose frequency matches the difference in energy levels $\Delta E = E_{n'} - E_n$. Within the harmonic oscillator approximation, ***transitions are only allowed between adjacent energy levels***, with $\Delta n = \pm 1$:

- for *absorption* of light, $n \to n' = n + 1$
- for *emission* of light, $n \to n' = n - 1$.

These rules that determine which states can be reached by optical transitions are called *selection rules.*

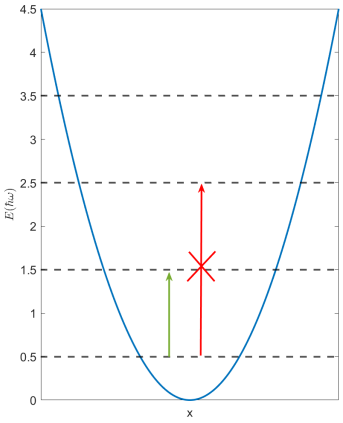
An additional rule for infrared spectroscopy is that the ***dipole moment of the molecule must change as it undergoes vibrational motion*** – otherwise that vibration is not infrared-active. This rule is usually summarized as $\frac{d\mu}{dR} > 0$.

To give a concrete example, homonuclear diatomic molecules like H_2 or O_2 have a dipole moment of zero, which remains zero as they vibrate. Homonuclear diatomics therefore have no infrared spectrum.

While we do not derive them here, these vibrational selection rules are derived in McQuarrie Section 5.12 for those interested.

For an IR-active vibration, the allowed transition energies for absorption of light are:

$$\Delta E = E_{n+1} - E_n = h\nu(\cancel{n} + 1 + \cancel{\tfrac{1}{2}}) - h\nu(\cancel{n} + \cancel{\tfrac{1}{2}}) = h\nu \tag{37}$$



which is independent of n! Because the harmonic oscillator has evenly spaced vibrational levels, all transitions fall at the same frequency, and our diatomic molecule can therefore only absorb light with the frequency (in Hertz) of:

$$\nu_{obs} = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \tag{38}$$

This frequency will also commonly be expressed in wavenumbers (cm^{-1}) as:

$$\tilde{\nu} = \frac{\nu_{obs}}{c} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{39}$$

Measuring a vibrational frequency in an infrared spectrum serves as a diagnostic, or fingerprint, of that molecule, since $\tilde{\nu}$ depends on the masses involved, as well as the bond strength k, which encodes whether the molecule features a single, double or triple bond.