

Chapter 4. The Harmonic Oscillator

Energy of a molecule is the sum of translational, rotational, vibrational and electronic energies.

Translational: kinetic energy of a motion of a molecule as a whole.

Rotational: for two-atomic molecule can be approximated as rigid, two-particle rotor.

Vibrational: for diatomic molecule can be approximated by a harmonic oscillator.

In this chapter, we will solve Schrodinger equation for a harmonic oscillator.

In this case, the potential energy is not constant, making Schrodinger equation a more complex differential equation. So, first we have to learn how to solve differential equations using power series.

Power-Series Solution of Differential Equations:

For example, a differential equation:

$$y''(x) + c^2 y(x) = 0$$

Power-Series Solution of Differential Equations:

Using the auxiliary equation, we have: $s^2 + c^2 = 0$

$$s = \pm ic$$

The solution is then: $y = c_1 e^{icx} + c_2 e^{-icx}$

Since: $e^{i\theta} = \cos \theta + i \sin \theta$

The solution can be written as: $y = A \cos cx + B \sin cx$

Now, we will use power series to solve the same equation. First, we assume that the solution can be expanded in Taylor series about $x=0$:

Taylor approximation theorem: Function f can be best approximated at $x=a$ by a polynomial:

$$P(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2}(x-a)^2 \dots$$

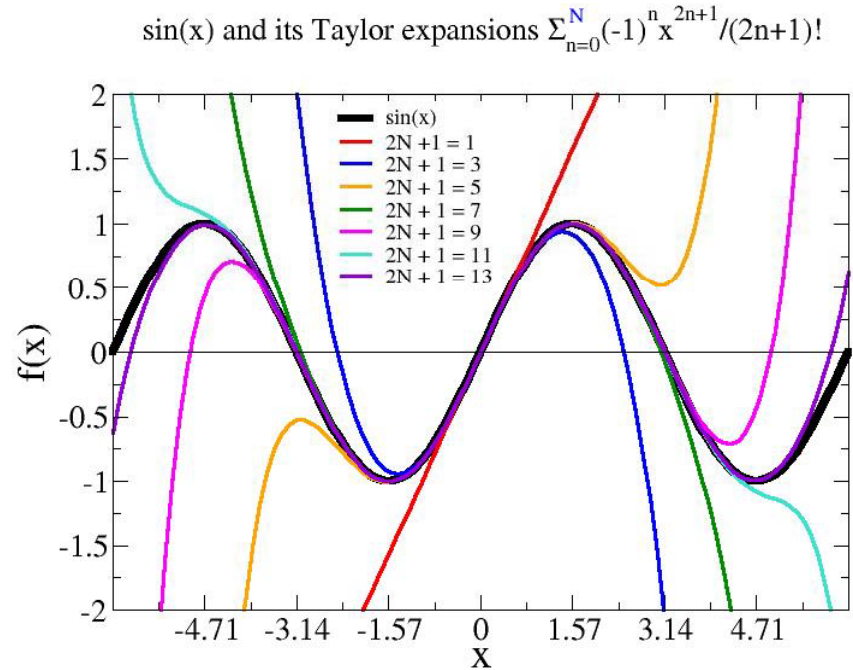
$$P(x) = \sum_{n=0}^N \frac{f^{(n)}(a)}{n!} (x-a)^n$$

Taylor Series (an example):

Obtain the Taylor series expansion about $x=0$ for $\sin x$.

First, we need to obtain the derivatives and their values for $a=0$:

$$\begin{array}{ll}
 f(x) = \sin x & f(0) = 0 \\
 f'(x) = \cos x & f'(0) = 1 \\
 f''(x) = -\sin x & \longrightarrow f''(0) = 0 \\
 f'''(x) = -\cos x & f'''(0) = -1 \\
 f^{iv}(x) = \sin x & f^{iv}(0) = 0
 \end{array}$$



$$P(x) = \sum_{n=0}^N \frac{f^{(n)}(a)}{n!} (x-a)^n = 0 + \frac{x}{1!} + 0 - \frac{x^3}{3!} + 0 + \frac{x^5}{5!} = \sum_{k=0}^{\infty} \frac{(-1)^k x^{2k+1}}{(2k+1)!}$$

Power-Series Solution of Differential Equations:

$$y''(x) + c^2 y(x) = 0$$

Now, we will use power series to solve the same equation. First, we assume that the solution can be expanded in Taylor series about $x=0$:

$$y(x) = a_0 + a_1 x + a_2 x^2 + \dots$$

$$y(x) = \sum_{n=0}^{\infty} a_n x^n$$

Differentiating, we have: $y'(x) = a_1 + 2a_2 x + 3a_3 x^2 + \dots$

$$y'(x) = \sum_{n=1}^{\infty} n a_n x^{n-1}$$

Second derivative gives: $y''(x) = 2a_2 + 3(2)a_3 x + \dots$

$$y''(x) = \sum_{n=2}^{\infty} n(n-1) a_n x^{n-2}$$

Power-Series Solution of Differential Equations:

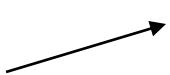
So, our differential equation becomes:

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} + \sum_{n=0}^{\infty} c^2 a_n x^n = 0$$

Next, we want to combine the sums using the following rule:

$$\sum_{j=0}^{\infty} b_j x^j + \sum_{j=0}^{\infty} c_j x^j = \sum_{j=0}^{\infty} (b_j + c_j) x^j$$

To use this rule, the summation limits in each sum of our expression need to be the same and the powers of x need to be the same. To do so, we need to modify the summation:

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} = \sum_{k=0}^{\infty} (k+2)(k+1)a_{k+2} x^k = \sum_{n=0}^{\infty} (n+2)(n+1)a_{n+2} x^n$$


Since the summation index is a dummy variable.

Power-Series Solution of Differential Equations:

- So, now we can combine sums:

$$\sum_{n=0}^{\infty} [(n+2)(n+1)a_{n+2} + c^2 a_n] \cdot x^n = 0$$

For this equation to be true for all values of x , the coefficients need to be zero

$$(n+2)(n+1)a_{n+2} + c^2 a_n = 0$$

$$a_{n+2} = -\frac{c^2 a_n}{(n+2)(n+1)}$$

So, if we know a_1 , we can get a_3, a_5 . If we know a_0 , we can get $a_2, a_4, a_6 \dots$. Since there is no restriction to the values of a_0 and a_1 , we give them values A and Bc :

$$a_0 = A$$

$$a_1 = Bc$$

The coefficients become:

$$a_0 = A$$

$$a_1 = Bc$$

$$a_2 = -\frac{c^2 A}{1 \cdot 2}$$

$$a_3 = -\frac{c^3 B}{2 \cdot 3}$$

$$a_4 = \frac{c^4 A}{4 \cdot 3 \cdot 2 \cdot 1}$$

$$a_5 = \frac{c^5 B}{5 \cdot 4 \cdot 3 \cdot 2}$$

$$a_{2k} = (-1)^k \frac{c^{2k} A}{(2k)!}$$

$$a_{2k+1} = (-1)^k \frac{c^{2k+1} B}{(2k+1)!}$$

So, our function becomes:

$$y = \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0,2,4}^{\infty} a_n x^n + \sum_{n=1,3,5}^{\infty} a_n x^n$$

$$y = A \sum_{k=0}^{\infty} (-1)^k \frac{c^{2k} x^{2k}}{(2k)!} + B \sum_{k=0}^{\infty} (-1)^k \frac{c^{2k+1} x^{2k+1}}{(2k+1)!}$$

The two series in the previous equation are the Taylor series for $\cos(cx)$ and $\sin(cx)$. Hence, the solution is:

$$y = A \cos(cx) + B \sin(cx)$$

The One-Dimensional Harmonic Oscillator

1. Classical Treatment: one particle with mass m attracted toward the origin by a force proportional to the particle's displacement from the origin:

$$F = -kx \quad k: \text{force constant}$$

From Newton's second law, $F=ma$, we have:

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

This differential equation is the same as the one on slide 1, with $c=(k/m)^{1/2}$. So, the solution is:

$$x = A \sin(2\pi\nu t + b)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

1D Harmonic Oscillator (classical treatment)

The potential energy can be determined from:

$$F = -\frac{dV}{dx} = -kx$$

$$V = \frac{1}{2}kx^2$$

The kinetic energy can be determined from:

$$E_k = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2$$
$$x = A\sin(2\pi\nu t + b)$$
$$\frac{dx}{dt} = 2\pi\nu A\cos(2\pi\nu t + b)$$

$$E_k = 2m\pi^2\nu^2 A^2 \cos^2(2\pi\nu t + b)$$

1-D Harmonic Oscillator (classical treatment)

So, the total energy will be:

$$E = V + E_k = \frac{1}{2}kx^2 + 2m\pi^2\nu^2 A^2 \cos^2(2\pi\nu t + b)$$

$$E = 2\pi^2\nu^2 mA^2 \sin^2(2\pi\nu t + b) + 2m\pi^2\nu^2 A^2 \cos^2(2\pi\nu t + b)$$

Since $\sin^2x + \cos^2x=1$, we have:

$$E = 2\pi^2\nu^2 mA^2$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

The Hamiltonian operator is:

$$\hat{H} = \hat{E} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + 2\pi^2\nu^2 mx^2 = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} - \alpha^2 x^2 \right)$$

$$\alpha = \frac{2\pi\nu m}{\hbar}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

The Schrodinger equation is:

$$\hat{H} \psi = E \psi$$
$$\frac{d^2 \psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \alpha^2 x^2 \right) \psi = 0$$

Before solving the equation using power series, it is useful to modify the form by using:

$$f(x) = e^{-\frac{\alpha x^2}{2}} \psi(x)$$
$$\psi(x) = e^{\frac{\alpha x^2}{2}} f(x)$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

Differentiating twice gives us:

$$\psi' = -\frac{2\alpha x}{2} e^{-\frac{\alpha x^2}{2}} f(x) + e^{-\frac{\alpha x^2}{2}} \cdot f'(x)$$

$$\psi'' = -\alpha e^{-\frac{\alpha x^2}{2}} f(x) - \alpha x \left(-\frac{2\alpha x}{2}\right) e^{-\frac{\alpha x^2}{2}} f(x) - \frac{2\alpha x}{2} e^{-\frac{\alpha x^2}{2}} \cdot f'(x)$$

$$-\frac{2\alpha x}{2} e^{-\frac{\alpha x^2}{2}} \cdot f'(x) + e^{-\frac{\alpha x^2}{2}} f''(x)$$

$$\psi'' = e^{-\frac{\alpha x^2}{2}} (-\alpha f(x) + \alpha^2 x^2 f(x) - 2\alpha x \cdot f'(x) + f''(x))$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

So, the Schrodinger equation becomes:

$$f''(x) - 2\alpha x f'(x) + \left(\frac{2mE}{\hbar^2} - \alpha\right) f(x) = 0$$

Now, we can do the power series:

$$f(x) = \sum_{n=0}^{\infty} c_n x^n$$

$$f'(x) = \sum_{n=1}^{\infty} c_n n x^{n-1} = \sum_{n=0}^{\infty} c_n n x^{n-1} \quad \text{Since the first term is zero}$$

$$f''(x) = \sum_{n=0}^{\infty} (n+2)(n+1)c_{n+2} x^n$$

So, the Schrodinger equation becomes:

$$\sum_{n=1}^{\infty} \left[(n+2)(n+1)c_{n+2} - 2\alpha n c_n + \left(\frac{2mE}{\hbar^2} - \alpha\right) c_n \right] x^n = 0$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

The coefficients again need to be zero, so:

$$c_{n+2} = \frac{\alpha + 2\alpha n - \frac{2mE}{\hbar^2}}{(n+2)(n+1)} c_n$$

We have two arbitrary constants, c_0 and c_1 . If we set c_1 to zero, the solution will have only even powers of x :

$$\psi = e^{-\frac{\alpha x^2}{2}} f(x) = e^{-\frac{\alpha x^2}{2}} \sum_{n=0,2,4,\dots}^{\infty} c_n x^n = e^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} c_{2l} x^{2l}$$

If we set c_0 to zero, the solution will have only odd powers of x :

$$\psi = e^{-\frac{\alpha x^2}{2}} f(x) = e^{-\frac{\alpha x^2}{2}} \sum_{n=1,3,5,\dots}^{\infty} c_n x^n = e^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} c_{2l+1} x^{2l+1}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

The general solution of the Schrodinger equation is a linear combination of these two equations:

$$\psi = Ae^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} c_{2l} x^{2l} + BAe^{-\frac{\alpha x^2}{2}} \sum_{l=0}^{\infty} c_{2l+1} x^{2l+1}$$

Now, we must see if any boundary conditions lead to restrictions to the solution. To do so, we examine the ratios of successive coefficients in each series:

$$\text{Even series: } \frac{c_{2l+2}}{c_{2l}} = \frac{\alpha + 4\alpha l - \frac{2mE}{\hbar^2}}{(2l+1)(2l+2)} = \frac{\alpha}{l} \leftarrow \text{For large } l$$

$$\text{Odd series: ratio is the same: } = \frac{\alpha}{l}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

Now let's look at the power series expansion for the function: $e^{\alpha x^2}$

$$e^z = \sum_{n=0}^{\infty} \frac{z^n}{n!}$$

$$e^{\alpha x^2} = \sum_{n=0}^{\infty} \frac{\alpha x^{2n}}{n!} = 1 + \alpha x^2 + \dots + \frac{\alpha^l x^{2l}}{l!} + \frac{\alpha^{l+1} x^{2l+1}}{(l+1)!} + \dots$$

The ratio of the coefficients in this series is:

$$\frac{\frac{\alpha^{l+1}}{(l+1)!}}{\frac{\alpha^l}{l!}} = \frac{\alpha}{l+1} \sim \frac{\alpha}{l}$$

The ratio is the same, so we conclude

that for large x , each series goes as $e^{\alpha x^2}$

So, ψ will behave as $e^{\alpha x^2}$ for large x

1-D Harmonic Oscillator (Quantum mechanical treatment)

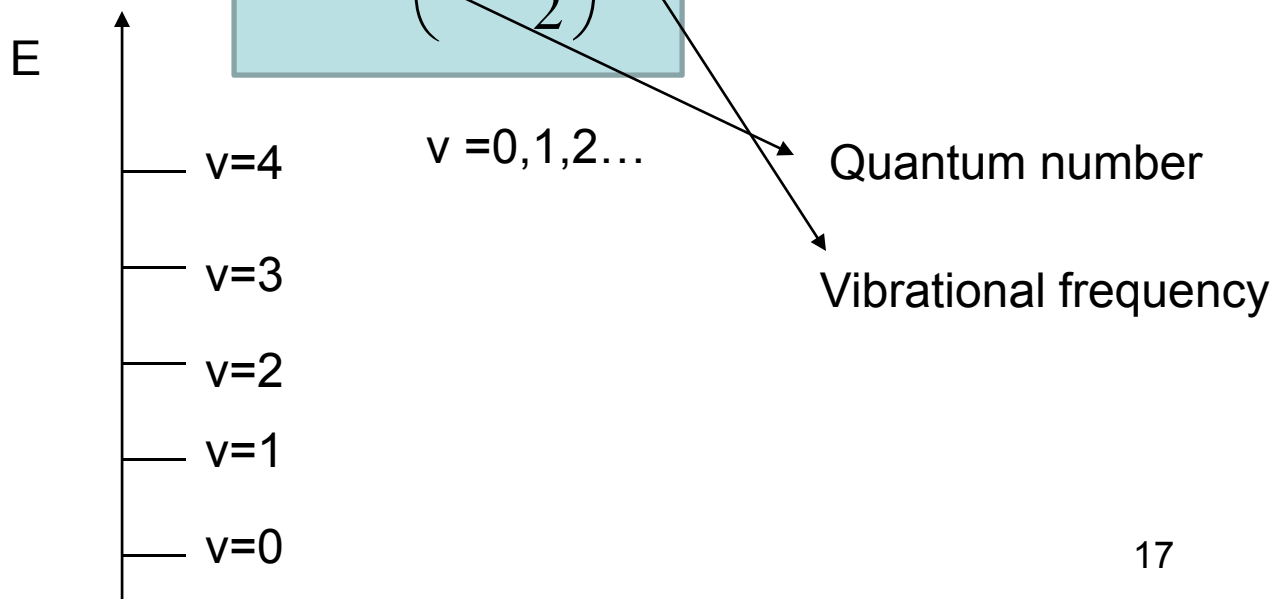
Problem: the wave-function becomes infinity as x goes to infinity. So, the wavefunction will not be quadratically integrable. To avoid this, we have to stop the series at some number n . For example, if coefficient becomes zero at some value $n=v$, the rest of the coefficients in the series would be zero. To accomplish this, we adjust energy E to make $c_v=0$:

$$c_{n+2} = \frac{\alpha + 2\alpha n - \frac{2mE}{\hbar^2}}{(n+2)(n+1)} c_n$$

$$\alpha + 2\alpha v - \frac{2mE}{\hbar^2} = 0 \quad \alpha = \frac{2\pi\nu m}{\hbar}$$

$$E = \left(v + \frac{1}{2} \right) h\nu$$

1. The harmonic oscillator energy levels are equally spaced.
2. Zero-point energy exists, which suggests that the molecules are not at rest even at zero kelvin.



1-D Harmonic Oscillator (Quantum mechanical treatment)

The recursion relation becomes:

$$c_{n+2} = \frac{2\alpha(n-v)}{(n+2)(n+1)} c_n$$

The wave functions are then:

$$\psi_v = \begin{cases} e^{-\frac{\alpha x^2}{2}} (c_0 + c_2 x^2 + \dots + c_v x^v) & \text{For } v \text{ even} \\ e^{-\frac{\alpha x^2}{2}} (c_1 x + c_3 x^3 + \dots + c_v x^v) & \text{For } v \text{ odd} \end{cases}$$

As in the particle in a box, it is the boundary condition that force us to quantize the energy.

1-D Harmonic Oscillator (Quantum mechanical treatment)

Even functions: $f(-x) = f(x)$

$$x^2$$

$$e^{-bx^2}$$

In this case, the function is symmetric about the y axis, and:

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

Odd functions: $f(-x) = -f(x)$

$$x$$

$$xe^{x^2}$$

$$\frac{1}{x}$$

$$x$$

$$\int_{-a}^a f(x)dx = 0$$

Let's consider the wave functions in more detail. The exponential factor $e^{\alpha x^2}$ is an even function of x . If v is even, the polynomial part of the equation is an even function, so the overall wave function is even. If v is odd, the wave function is also odd.

1-D Harmonic Oscillator (Quantum mechanical treatment)

The wave function for $v=0$:

$$\psi_0 = c_0 e^{-\frac{\alpha x^2}{2}}$$

We obtain c_0 by normalization:

$$\int_{-\infty}^{\infty} c_0^2 e^{-\alpha x^2} dx = 2c_0^2 \int_0^{\infty} e^{-\alpha x^2} dx = 1$$

From appendix:

$$\int_0^{\infty} e^{-bx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{b}}$$

$$2c_0^2 \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = 1$$

$$c_0 = \sqrt[4]{\frac{\alpha}{\pi}}$$

The wave function for $v=0$ is then:

$$\psi_0 = \sqrt[4]{\frac{\alpha}{\pi}} e^{-\frac{\alpha x^2}{2}}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

For $v=1$:

$$\psi_1 = c_1 x e^{-\frac{\alpha x^2}{2}}$$

Again, the coefficient c_1 is obtained from normalization:

$$\int_{-\infty}^{\infty} c_1^2 x^2 e^{-\alpha x^2} dx = 2c_1^2 \int_0^{\infty} x^2 e^{-\alpha x^2} dx = 1$$

From appendix:

$$\int_0^{\infty} x^{2n} e^{-bx^2} dx = \frac{1 \cdot 3 \cdot \dots \cdot (2n-1)}{2^{n+1}} \sqrt{\frac{\pi}{b^{2n+1}}}$$

$$2c_1^2 \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}} = 1$$

$$c_1 = 2^{\frac{1}{2}} \alpha^{\frac{3}{4}} \pi^{-\frac{1}{4}}$$

So, the wave function for $v=1$ is:

$$\psi_1 = 2^{\frac{1}{2}} \alpha^{\frac{3}{4}} \pi^{-\frac{1}{4}} x e^{-\frac{\alpha x^2}{2}}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

For $v=2$:

$$\psi_2 = (c_0 + c_2 x^2) e^{-\frac{\alpha x^2}{2}}$$

From recursion relation:

$$c_{n+2} = \frac{2\alpha(n-v)}{(n+2)(n+1)} c_n \longrightarrow c_2 = \frac{2\alpha(0-2)}{(0+2)(0+1)} c_0 = -2\alpha c_0$$

So, the wave function is:

$$\psi_2 = c_0 (1 - 2\alpha x^2) e^{-\frac{\alpha x^2}{2}}$$

The c_0 in Ψ_2 is not the same as c_0 in Ψ_1 . It needs to be evaluated by normalization:

$$\int_{-\infty}^{\infty} c_0^2 (1 - 2\alpha x^2)^2 e^{-\alpha x^2} dx = 2c_0^2 \int_0^{\infty} (1 - 4\alpha x^2 + 4\alpha^2 x^4) e^{-\alpha x^2} dx = 1$$

$$2c_0^2 \left[\int_0^{\infty} e^{-\alpha x^2} dx - 4\alpha \int_0^{\infty} x^2 e^{-\alpha x^2} dx + 4\alpha^2 \int_0^{\infty} x^4 e^{-\alpha x^2} dx \right] = 1$$

1-D Harmonic Oscillator (Quantum mechanical treatment)

$$2c_0^2 \left[\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} - 4\alpha \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}} + 4\alpha^2 \frac{1 \cdot 3}{2^3} \sqrt{\frac{\pi}{\alpha^5}} \right] = 1$$

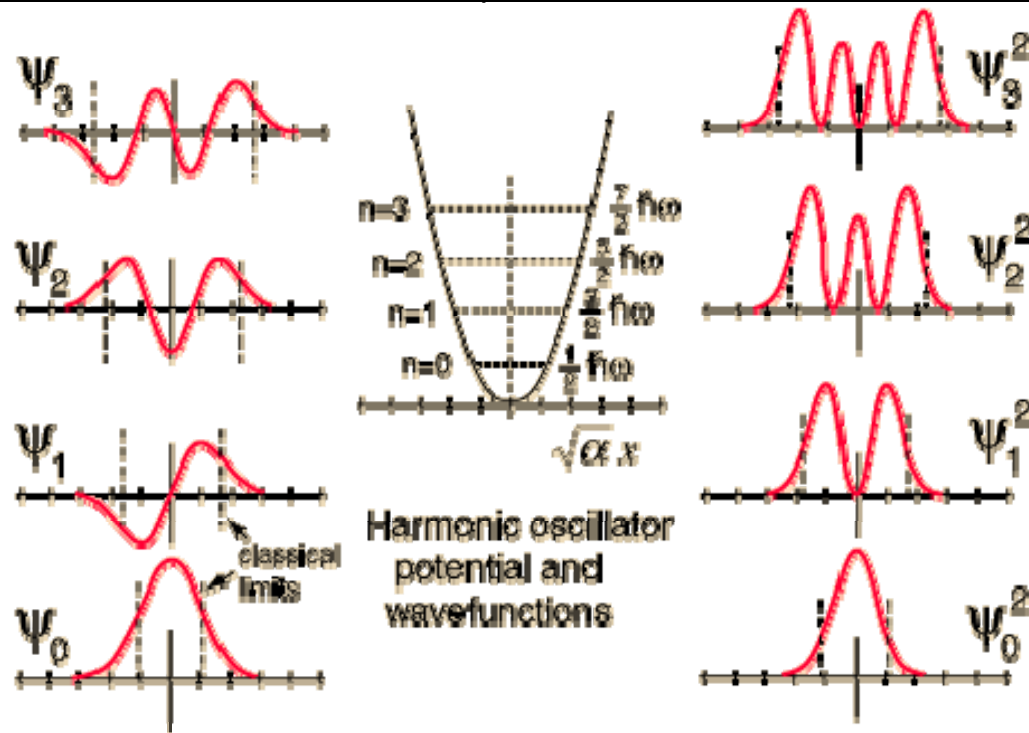
$$2c_0^2 \left[\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} - \sqrt{\frac{\pi}{\alpha}} + \frac{3}{2} \sqrt{\frac{\pi}{\alpha}} \right] = 1$$

$$c_0 = \sqrt[4]{\frac{\alpha}{4\pi}}$$

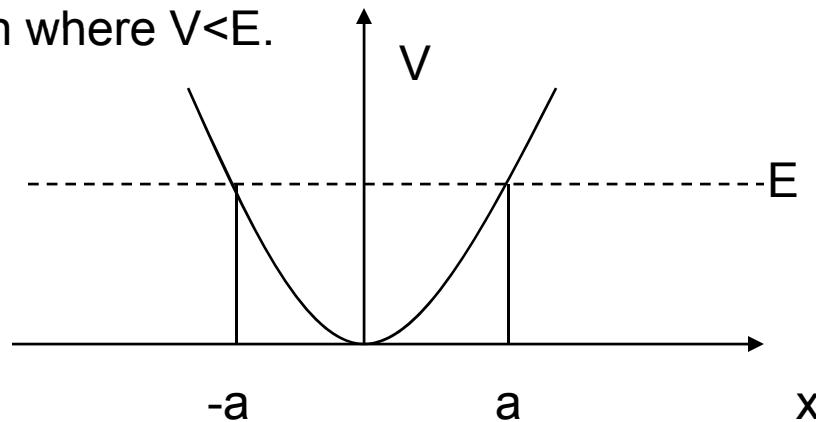
So, the wave function for $v=2$ is:

$$\psi_2 = \sqrt[4]{\frac{\alpha}{4\pi}} (1 - 2\alpha x^2) e^{-\frac{\alpha x^2}{2}}$$

1-D Harmonic Oscillator (Quantum mechanical treatment)



- The number of nodes equals the quantum number v .
- According to quantum-mechanical solution, there is some probability of finding a particle anywhere on x -axis. According to classical solution, the particle can be found only in the region where $V < E$.



1-D Harmonic Oscillator (Quantum mechanical treatment)

The classically-allowed region ($V < E$) for harmonic oscillator is:

$$E = \left(\nu + \frac{1}{2}\right)h\nu$$

$$V = 2\pi^2\nu^2mx^2$$

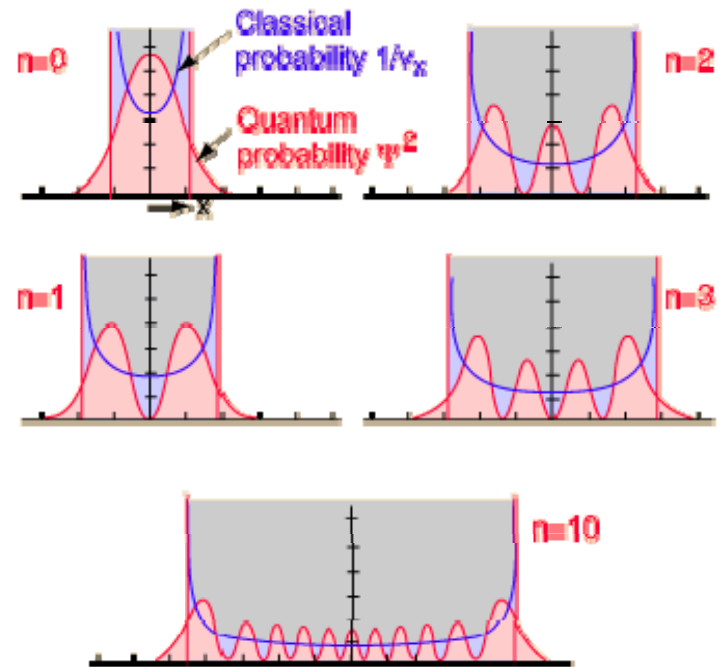
$$V < E$$

$$2\pi^2\nu^2mx^2 < \left(\nu + \frac{1}{2}\right)h\nu$$

$$x^2 < \frac{\left(\nu + \frac{1}{2}\right)h}{2\pi^2\nu m}$$

$$\alpha = \frac{2\pi\nu m}{\hbar}$$

$$-(2\nu + 1)^{\frac{1}{2}} \leq \alpha^{\frac{1}{2}}x \leq (2\nu + 1)^{\frac{1}{2}}$$

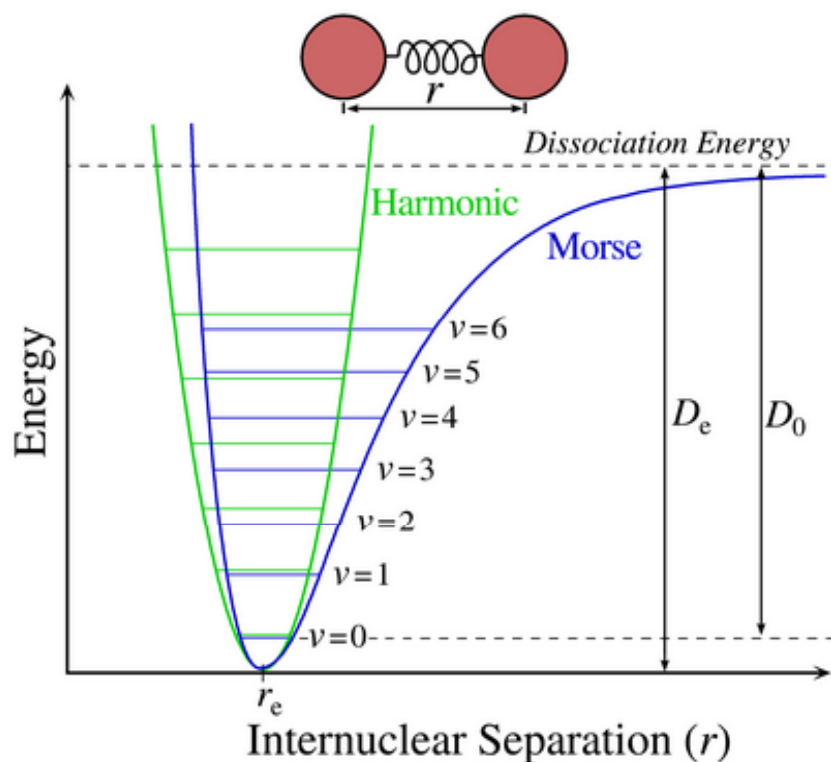


With higher quantum number, the maximum probability is farther from the origin. Classical and quantum description become more alike for larger quantum numbers.

Vibration of Molecules

- Electrons and nuclei can be treated separately.
- We first solve S. equation for electronic energy U at all positions of nuclei $U=U(R)$.
- Then we solve S. equation for nuclear motion using $U(R)$ as the potential energy.
- The energy of the system is the sum of E_k for translational motion and energy of internal motion of particles relative to each other.

For diatomic molecule: internal energy is sum of vibrational energy of two nuclei and their rotational energy. They can be treated separately. Here we consider vibrations.



We can see that the pot. energy for vibration of a diatomic molecule can be well approximated by pot. energy for harmonic oscillator.

$$E_{vib} = \left(v + \frac{1}{2}\right) h \nu_e$$

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

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

$$k = \left. \frac{d^2 U}{dR^2} \right|_{R=R_e}$$

Vibration of Molecules

As quantum number increases, the potential energy substantially deviates from the harmonic oscillator approximation. Instead of being equally spaced, vibrational energy levels become closer and closer to each other.

Eventually, the vibrational energy is large enough for molecule to dissociate: diatomic molecule has a finite number of vibrational levels, unlike harmonic oscillator.

A more accurate expression that accounts for anharmonicity is:

$$E_{vib} = \left(v + \frac{1}{2}\right)h\nu_e - \left(v + \frac{1}{2}\right)^2 h\nu_e x_e$$

-Using the time-dependent S. equation, one finds that the most probable vibrational transitions are for $\Delta v = \pm 1$.

-For absorption or emission, the vibration must change the molecule's dipole moment. So, H_2 and O_2 cannot absorb energy to undergo vibrational transition.

-The energy for vibrations falls in the mid-IR region.

- Overtones also appear, but they are weak.

-The relative population of two molecular energy levels is given by Boltzmann distribution law:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{\frac{-(E_i - E_j)}{kT}}$$

Here, g is the degeneracy of the level: for a non-degenerate level, $g=1$. For small diatomics, only $v=0$ level is populated. But, for heavy molecules such as I_2 , there is significant population of one or more vibrational excited states.

Vibration of Molecules

Example: The $v=0 \rightarrow 1$ band of LiH occurs at 1359 cm^{-1} . Calculate the ratio of the $v=1$ to $v=0$ populations at $25 \text{ }^\circ\text{C}$ and at $200 \text{ }^\circ\text{C}$.

$$\tilde{\nu} = 1359 \text{ cm}^{-1}$$

$$\Delta E = hc\tilde{\nu} = 6.62 \cdot 10^{-34} \text{ J} \cdot 3 \cdot 10^{10} \text{ cm/s} \cdot 1359 \text{ cm}^{-1} = 2.7 \cdot 10^{-20} \text{ J}$$

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{\frac{-(E_i - E_j)}{kT}} = e^{\frac{2.7 \cdot 10^{-20} \text{ J}}{1.38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}} = 0.0017 \quad \text{At } 25 \text{ }^\circ\text{C}$$

$$\frac{N_i}{N_j} = 0.016 \quad \text{At } 200 \text{ }^\circ\text{C}$$

Numerical Solution of the 1D Time Independent Schrodinger Equation

S. equation can be solved analytically for the particle in a box and the harmonic oscillator. For many potential energy functions, one particle, 1D S. equation can be solved only numerically.

Numerov Method

Taylor series for a function $f(x)$:

$$f(x) = f(a) + \frac{f'(a)(x-a)^1}{1!} + \frac{f''(a)(x-a)^2}{2!} + \dots$$

Let $a=x_n$ and $s=x-a=x-x_n$:

$$f(x_n + s) = f(x_n) + \frac{f'(x_n)(s)^1}{1!} + \frac{f''(x_n)s^2}{2!} + \frac{f'''(x_n)s^3}{3!} + \frac{f^{(iv)}(x_n)s^4}{4!} + \frac{f^{(v)}(x_n)s^5}{5!}$$

Replacement of s by $-s$ gives:

$$f(x_n - s) = f(x_n) - \frac{f'(x_n)(s)^1}{1!} + \frac{f''(x_n)s^2}{2!} - \frac{f'''(x_n)s^3}{3!} + \frac{f^{(iv)}(x_n)s^4}{4!} - \frac{f^{(v)}(x_n)s^5}{5!}$$

Numerov Method

Addition of the last two equations gives:

$$f(x_n + s) + f(x_n - s) = 2f(x_n) + f''(x_n)s^2 + \frac{f^{(iv)}(x_n)s^4}{12}$$

- We neglected the terms higher than s^5 . This is ok for small s .
- In solving the S. equation numerically, we will divide the x axis into small intervals, each of length s . We relabel things as follows:

$$f_{n-1} = f(x_n - s)$$

$$f_n = f(x_n)$$

$$f_{n+1} = f(x_n + s)$$

The addition equation becomes:

$$f_{n+1} + f_{n-1} = 2f_n + f''_n s^2 + \frac{f^{(iv)}_n s^4}{12}$$

The n subscript means that the functions are evaluated at point x_n .

$$f_{n+1} = -f_{n-1} + 2f_n + f''_n s^2 + \frac{f^{(iv)}_n s^4}{12}$$

Numerov Method

Replacing f by wave function Ψ , we have:

$$\psi_{n+1} = -\psi_{n-1} + 2\psi_n + \psi''_n s^2 + \frac{\psi^{(iv)}_n s^4}{12}$$

So, we need the second and fourth derivative of Ψ . The S. equation gives:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\psi'' = \underbrace{\frac{m}{\hbar^2} (2V - 2E)}_G \psi$$

To obtain the fourth derivative ($\Psi^{(iv)}s^4$), we use the equation:

$$f_{n+1} = -f_{n-1} + 2f_n + f''_n s^2 + \frac{f^{(iv)}_n s^4}{12}$$

Here, we replace f by Ψ'' and multiply the resulting equation by s^2 :

$$\psi''_{n+1} = -\psi''_{n-1} + 2\psi''_n + \psi^{(iv)}_n s^2 + \frac{\psi^{(vi)}_n s^4}{12}$$

Neglect the sixth derivative and multiply by s^2 .

$$\psi''_{n+1} s^2 = -\psi''_{n-1} s^2 + 2\psi''_n s^2 + \psi^{(iv)}_n s^4$$

Numerov Method

$$\psi^{(iv)}_n s^4 = \psi''_{n+1} s^2 + \psi''_{n-1} s^2 - 2\psi''_n s^2$$

Substitution of the S. equation $\Psi'' = G \Psi$ gives:

$$\psi^{(iv)}_n s^4 = G_{n+1} \psi_{n+1} s^2 + G_{n-1} \psi_{n-1} s^2 - 2G_n \psi_n s^2$$

Substituting these derivatives into our Taylor sum, we get:

$$\psi_{n+1} = -\psi_{n-1} + 2\psi_n + \psi''_n s^2 + \frac{\psi^{(iv)}_n s^4}{12}$$

$$\psi_{n+1} = -\psi_{n-1} + 2\psi_n + G_n \psi_n s^2 + \frac{G_{n+1} \psi_{n+1} s^2 + G_{n-1} \psi_{n-1} s^2 - 2G_n \psi_n s^2}{12}$$

Solving equation for Ψ_{n+1} , we get:

$$\psi_{n+1} = \frac{2\psi_n - \psi_{n-1} + \frac{5G_n \psi_n s^2}{6} + \frac{G_{n-1} \psi_{n-1} s^2}{12}}{\frac{1 - G_{n+1} s^2}{12}}$$

This equation allows us to calculate Ψ_{n+1} , if we know Ψ_n and Ψ_{n-1} .

Numerov Method

How to use the Numerov method:

1. We guess the value for energy E .
2. At x_0 (classically forbidden region), we set $\Psi_0=0$.
3. We divide x into small intervals, say $s=0.0001$.
4. We pick at x_{0+s} to be small: $\Psi_{x_{0+s}}=0.0001$.
5. We solve the Numerov equation for $n=1$.
6. We want x_{\max} to be $\Psi_{x_{\max}}=0$ and the number of nodes to be zero (for ground state).
7. We keep guessing E until we satisfy conditions under 6.

Dimensionless Variables:

What energies should we use as a guess in the Numerov method: 10^{-20} J, 10^{-15} J..?

To answer this question, we reformulate S. equation using dimensionless variables, taking the harmonic oscillator as the example.

We seek for energy and coordinate x to have no units:

$$E_r = \frac{E}{A}$$

$$x_r = \frac{x}{B}$$

Dimensionless Variables:

The dimensions of energy are mass x length² x time⁻²: $[E]=ML^2T^{-2}$.

For harmonic oscillator: $V=kx^2/2$. Since x has dimension of length and the dimensions of energy are listed above, the dimensions of k are: $[k]=MT^{-2}$.

For mass: $[m]=M$; for \hbar , the units are: $[\hbar]=ML^2T^{-1}$.

Let $A=m^a k^b \hbar^c$:

$$[A] = [m^a k^b \hbar^c] = M^a (MT^{-2})^b (ML^2T^{-1})^c = M^{a+b+c} L^{2c} T^{-2b-c}$$

$$a + b + c = 1$$

$$2c = 2$$

$$-2b - c = -2$$

So, the solution is: $A=m^{-1/2}k^{1/2} \hbar$

Let $B=m^d k^e \hbar^f$. B needs to be: $B=m^{-1/4}k^{-1/4} \hbar^{1/2}$.

So, the reduced variables are:

$$E_r = \frac{E}{m^{-\frac{1}{2}} k^{\frac{1}{2}} \hbar}$$

$$x_r = \frac{x}{m^{-\frac{1}{4}} k^{-\frac{1}{4}} \hbar^{\frac{1}{2}}}$$

Dimensionless Variables:

Using $k^{1/2}=2\pi\nu m^{1/2}$ and $\alpha=2\pi\nu m/\hbar$, we have the alternative expression:

$$E_r = \frac{E}{h\nu}$$
$$x_r = \alpha^2 x$$

Since $\int \Psi^2 dx$ is the probability, it needs to be dimensionless. So, the wave function Ψ must have the dimensions of length^{-1/2}. Since B has units of length:

$$\psi_r = \frac{\psi}{B^{-1/2}}$$

We now rewrite the S. equation in terms of reduced variables:

$$\frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2} B^{-1/2} \psi_r = B^{-1/2} \frac{d}{dx} \frac{d\psi_r}{dx} = B^{-1/2} \frac{d}{dx} \frac{d\psi_r}{dx_r} \frac{dx_r}{dx} = B^{-1/2} \frac{d}{dx_r} \frac{d\psi_r}{dx_r} \frac{dx_r}{dx} \frac{dx_r}{dx}$$

Since $x_r=x/B$, $dx_r=dx/B$ and $dx_r/dx=B^{-1}$. Thus, we have:

$$\frac{d^2\psi}{dx^2} = B^{-5/2} \frac{d^2}{dx_r^2} \psi_r =$$

Dimensionless Variables:

The harmonic oscillator equation is:

$$\begin{aligned}
 & -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad \longrightarrow \quad \text{With dimensions} \\
 & -\frac{\hbar^2}{2m} B^{-\frac{5}{2}} \frac{d^2\psi_r}{dx_r^2} + \frac{1}{2} kx_r B^2 B^{-\frac{1}{2}} \psi_r = AE_r B^{-\frac{1}{2}} \psi_r \quad \longrightarrow \quad \text{Without dimensions}
 \end{aligned}$$

Division by $B^{-1/2}$ and substitution of A and B constants gives:

$$\begin{aligned}
 & -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \\
 & -\frac{\hbar^2}{2m} m^{\frac{1}{2}} k^{\frac{1}{2}} \hbar^{-1} \frac{d^2\psi_r}{dx_r^2} + \frac{1}{2} kx_r m^{-\frac{1}{2}} k^{-\frac{1}{2}} \hbar \psi_r = m^{-\frac{1}{2}} k^{\frac{1}{2}} \hbar E_r \psi_r \\
 & \frac{d^2\psi_r}{dx_r^2} = \underbrace{(x_r^2 - 2E_r)}_{G_r} \psi_r
 \end{aligned}$$

Dimensionless Variables:

- Now, we can expect lowest energy eigenvalue to be on the order of 1.
- We can use Numerov method for relative values using intervals $s_r=s/B$.

Choice of $x_{r,0}$, $x_{r,max}$ and s_r :

Suppose we want to find all the harmonic oscillator eigenvalues and eigenfunctions with $E_r < 5$. We need to find classically-forbidden regions (when $E_r = V_r$):

$$V_r = \frac{V}{m^{-\frac{1}{2}} k^{\frac{1}{2}} \hbar} = \frac{\frac{1}{2} k x^2}{m^{-\frac{1}{2}} k^{\frac{1}{2}} \hbar} = \frac{\frac{1}{2} k^{\frac{1}{2}} x_r^2 m^{-\frac{1}{2}} k^{-\frac{1}{2}} \hbar}{m^{-\frac{1}{2}} \hbar} = \frac{1}{2} x_r^2$$

So, for $E_r=5$, $x_r=-3.16$ to $+3.16$. So, it's reasonable to use a range for x_r of -5 to $+5$. For reasonable accuracy, we need ~ 100 points, so $s_r=0.1$

Using Excel Spreadsheet for the Numerov Method:

1. In cell A1, put a title: Numerov Method for Schrodinger equation, $V=0.5kx^2$
2. In cell A3 enter $E_r=$
3. In cell B3 enter 0 (our initial guess for energy)
4. In cell C3 enter $s_r=$
5. In cell D3 enter 0.1
6. In cell A5 enter x_r
7. In cell B5 enter G_r
8. In cell C5 enter $\psi_{s,r}$
9. In cell A7 enter -5
10. In cell A8 enter $=A7+D3$
11. Copy cell A8 and paste in cells A9-A107
12. In cell B7 enter $=A7^2-2*B3$
13. Copy cell B7 and paste in cells B8-B107
14. In cell C7 enter 0
15. In cell C8 enter $1E-4$
16. In cell C9, enter:
$$=(2*C8-C7+5*B8*C8*D3^2/6+B7*C7*D3^2/12)/(1-B9*D3^2/12)$$
17. Copy cell C9 and paste in cells C10-C107.
18. In cell D9 enter $=IF(C9*C8<0,1,0)$
19. Copy cell D9 and paste in cells D10-D107.
20. In cell E2 enter nodes=
21. In cell F2 enter $=SUM(D9:D107)$

Using Excel Spreadsheet for the Numerov Method:

22. Select cells A7-A107 and C7-C107
23. Insert-Chart-XY Scatter
24. Change Eguess until you have 0 nodes (for ground state) and the wave function is zero at $x_r > 5$. The solution should be at $E_{\text{guess}} = 0.5$.
25. If you want program to do the guessing for you: Tools-Solver: In "Set Target Cell Box", enter $\$C\107 ; In Value, put 0. In "By Changing Cells Box" enter $\$B\3 . Click Solve.