Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 13

Oct 2nd, 2013

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Objectives

- To motivate the study of vibrational spectroscopy.
- To review the classical harmonic oscillator.
- To present the Schrödinger equation for the quantum harmonic oscillator.
- To present the eigenfunctions and eigenvalues of the quantum harmonic oscillator.
- To present the parity of the eigenfunctions of the quantum harmonic oscillator.

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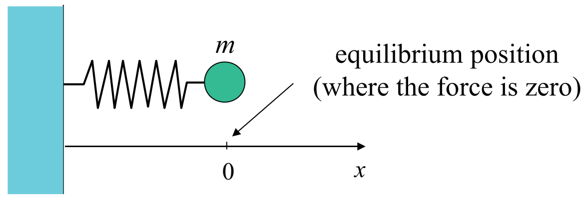
Classical harmonic oscillator

The classical harmonic oscillator is a body of mass m brought in periodic motion by a restoring force which obeys Hooke's law.



The force is given by Hooke's law:

$$F(x) = -kx$$

k is called the force constant

The potential is found by integrating the equation $F = -dV/dx$

$$V(x) = -\int F(x)\,dx = -\int(-kx)\,dx = \frac{1}{2}kx^2 + \text{const}$$

we choose const=0

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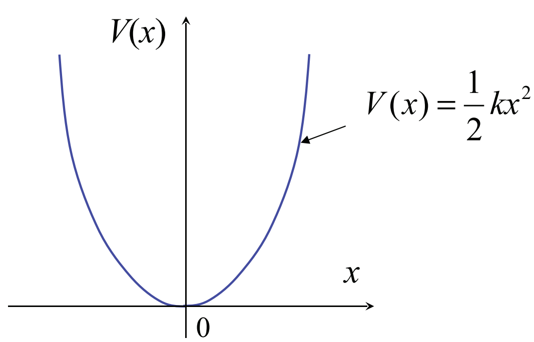
Potential energy curve for a harmonic oscillator

Equivalently, we can define the harmonic oscillator as a particle moving in a parabolic potential:



The harmonic oscillator is a model system that is key to understanding vibrational spectroscopy of diatomic molecules.

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Classical treatment harmonic oscillator

Newton's equation is

$$ma = F$$

In fact, this is a differential equation

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

which we can write as

$$\frac{d^2x}{dt^2} + \omega^2 x = 0, \qquad \text{where} \quad \omega = \sqrt{\frac{k}{m}}$$

The general solution of this equation is

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

ω is the oscillation frequency in radians per second.

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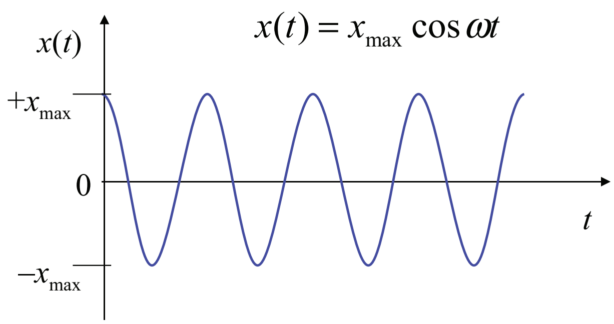
Classical trajectory the harmonic oscillator

Suppose that the initial position is $x(t=0) = x_{\max}$.
Then $B = 0$ and $A = x_{\max}$, so the solution becomes

$$x(t) = x_{\max}\cos\omega t$$



The name "harmonic" refers to the fact that the displacement of the mass changes (co)sinusoidally ("harmonically") as a function of time.

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Quantum-mechanical treatment of a harmonic oscillator

The Hamiltonian for a harmonic oscillator is given by

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} + \frac{1}{2} k x^2$$

which induces the following Schrödinger equation

$$-\frac{\hbar^2}{2m} \cdot \frac{d^2 \psi(x)}{dx^2} + \frac{1}{2} k x^2 \psi(x) = E \psi(x)$$

The solutions of this equation are not easily found. One particular technique to solve it is by power series. Here we just present the solutions and discuss them.

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Solutions to the quantum-mechanical harmonic oscillator

The **eigenfunctions** and **eigenvalues** of the harmonic oscillator are

$$\psi_n(x) = \left[2^n \cdot n!\right]^{-1} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} H_n\left(\sqrt{\alpha}\, x\right)$$

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \ ; \ \alpha = \sqrt{\frac{mk}{\hbar^2}}$$

where the **Hermite polynomials** are given by

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n}\left(e^{-y^2}\right)$$

which can also be determined recursively

$$H_{n+1}(y) = 2y H_n(y) - 2n H_{n-1}(y)$$
$$H_n'(y) = 2n H_{n-1}(y)$$

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First four harmonic oscillator eigenfunctions and their eigenvalues

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad E_0 = \frac{1}{2}\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \qquad E_1 = \frac{3}{2}\hbar\omega$$

Two equivalent expressions for the coefficient α

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2} \qquad E_2 = \frac{5}{2}\hbar\omega$$

$$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4} \left(2\alpha x^3 - 3x\right) e^{-\alpha x^2/2} \qquad E_3 = \frac{7}{2}\hbar\omega$$

$$\boxed{\alpha = \frac{\omega m}{\hbar} \qquad \alpha = \frac{\sqrt{km}}{\hbar}}$$

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Energy levels of the quantum harmonic oscillator

In general, the eigenvalues of the Schrödinger equation for the harmonic oscillator have the form

$$\boxed{E_n = \hbar\omega\left(n + \tfrac{1}{2}\right), \qquad n = 0, 1, 2, 3, \ldots \qquad \omega = \left(\frac{k}{m}\right)^{1/2}}$$

where ω is the frequency of vibrations in **radians** per second and k is the force constant.

Equivalent expression:

$$\boxed{E_n = h\nu\left(n + \tfrac{1}{2}\right), \qquad n = 0, 1, 2, 3, \ldots \qquad \nu = \frac{\omega}{2\pi}}$$

where ν is the frequency of vibrations in cycles per second

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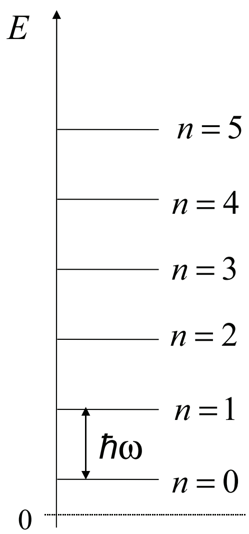
Energy level diagram for the quantum harmonic oscillator



$$E_n = \hbar\omega\left(n+\tfrac{1}{2}\right) = h\nu\left(n+\tfrac{1}{2}\right), \quad n = 0, 1, 2, 3, \ldots$$

Energy levels are spaced equally:

$$\text{spacing} = \hbar\omega = h\nu$$

The ground state has the quantum number n=0, not n=1 as was the case for a particle in a one-dimensional box.

The zero-point energy is positive:

$$E_0 = \frac{\hbar\omega}{2} \longleftarrow$$ vibrational zero-point energy

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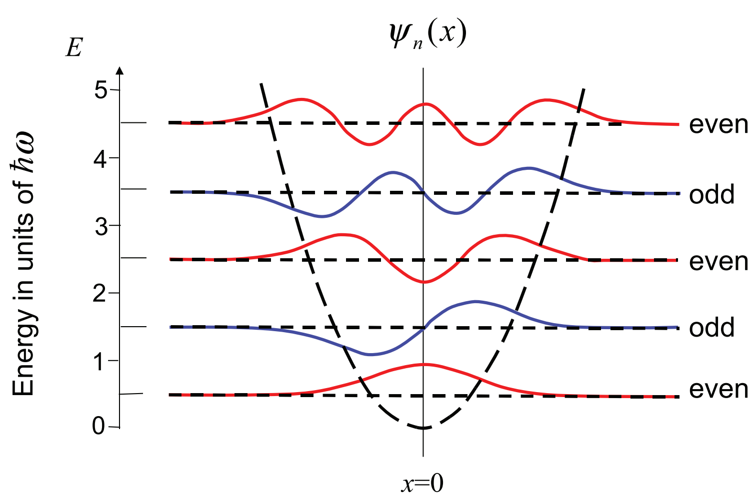
Parity of harmonic oscillator wave-functions

The harmonic oscillator wave functions with n=odd are odd, functions with n=even are even.



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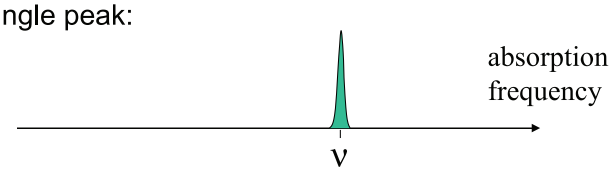
Selection rules for harmonic oscillator transitions

Using advanced quantum theory one can show that the probability (and hence intensity) of a transition between states ψ_m and ψ_n is proportional to

$$I_{n\leftrightarrow m} \propto \left| \int_{-\infty}^{\infty} \psi_n^* x \psi_m \, dx \right|^2$$

One can also show that for the harmonic oscillator wave functions, the above integral vanishes unless $n = m \pm 1$.

This means that absorption the spectrum of a harmonic oscillator consists of a single peak:



$$\Delta E = h\nu\left(n+1+\tfrac{1}{2}\right) - h\nu\left(n+\tfrac{1}{2}\right) = h\nu, \quad \text{where} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Integrals involving harmonic oscillator wave-functions

Consider the integral

$$I = \int_{-\infty}^{\infty} e^{-bx^2} \, dx = \left(\frac{\pi}{b}\right)^{1/2} \qquad (1)$$

Let us treat I as a function of b and differentiate it with respect to b

LHS: $$\frac{dI}{db} = \frac{d}{db}\int_{-\infty}^{\infty} e^{-bx^2} \, dx = -\int_{-\infty}^{\infty} x^2 e^{-bx^2} \, dx$$

RHS: $$\frac{dI}{db} = \frac{d}{db}\left(\frac{\pi}{b}\right)^{1/2} = -\frac{1}{2b}\left(\frac{\pi}{b}\right)^{1/2}$$

Therefore,

$$\int_{-\infty}^{\infty} x^2 e^{-bx^2} \, dx = \frac{1}{2b}\left(\frac{\pi}{b}\right)^{1/2} \qquad (2)$$

Exercise. Using Eqs. (1) and (2) verify that the harmonic oscillator eigenfunctions $\psi_0(x)$ and $\psi_1(x)$ are normalized.