Quantum Mechanics: Vibration and Rotation of Molecules

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I. 1-Dimensional Classical Harmonic Oscillator

The classical picture for motion under a harmonic potential (mass attached to spring attached to surface; two massess connected by spring) is determined by solutions to Newton's equations of motion:

$$F = ma = m\frac{d^2x}{dx^2} = -\frac{dV(x)}{dx} = -kx$$

where k is a force constant for the spring connecting the masses, and $V(x) = \frac{1}{2}kx^2$ is the harmonic potential (Hooke's Law),and vector notation has been dropped for this one-dimensional case. General solutions to this equation are of the form:

$$x = x_M \, cos(\omega_0 t - \phi)$$

The behavior of the amplitude, or deviation from equilibrium separation, is sinusoidally varying with amplitude x_M and angular frequency ω_0. ω_0 is related to the mass and force constant through the relation $\omega_0 = \sqrt{\frac{k}{m}}$.

The kinetic energy of the mass is $T = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{p^2}{2m}$ with $p = m\frac{dx}{dt}$ being the particle momentum.

The **total energy** is then (recalling that $k = m\omega_0^2$):

$$E = T + V(x) = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}\,m\omega_0^2x^2$$

Substituting the general solution equation discussed above, we see that the total energy is independent of time (as required for conservative systems):

$$E = \frac{1}{2}m\omega_0^2 x_M^2$$

Thus, the energy is non-zero, continuous, and constant. The maximum displacement is related to the energy as $x_M = \sqrt{\frac{2E}{m\omega_0^2}}$.

Aside: Though we will not consider the following in terms of reduced mass for an oscillator (or rigid rotor when considering angular momentum), we present here the reducee mass for reference.

Reduced mass is the effective inertial mass appearing in the two-body problem of Newtonian mechanics. This is a quantity with the units of mass, which allows the two-body problem to be solved as if it were a one-body problem. Note however that the mass determining the gravitational force is not reduced. In the computation one mass can be replaced by the reduced mass, if this is compensated by replacing the other mass by the sum of both masses.

Given two bodies, one with mass m_1, and the other with mass m_2, they will orbit the barycenter of the two bodies. The equivalent one-body problem, with the position of one body with respect to the other as the unknown, is that of a single body of mass

$m_{red} = \mu = \frac{1}{\frac{1}{m_1}+\frac{1}{m_2}} = \frac{m_1 m_2}{m_1+m_2}$

where the force on this mass is given by the gravitational force between the two bodies. This can be proven easily. Use Newton's second law, the force exerted by body 2 on body 1 is

$F_{12} = m_1 a_1$.

The force exerted by body 1 on body 2 is

$F_{21} = m_2 a_2$.

According to Newton's third law, for every action there is an equal and opposite reaction:

$F_{12} = -F_{21}$.

Therefore,

$m_1 a_1 = -m_2 a_2$.

and

$a_2 = -\frac{m_1}{m_2}a_1$.

The relative acceleration between the two bodies is given by

$a = a_1 - a_2 = (1 + \frac{m_1}{m_2})a_1 = (\frac{m_2+m_1}{m_1 m_2})m_1 a_1 = F_{12}/m_{red}$.

So we conclude that body 1 moves with respect to the position of body 2 as a body of mass equal to the reduced mass.

The reduced mass is frequently denoted by the Greek letter μ .

2

Applying the gravitational formula we get that the position of the first body with respect to the second is governed by the same differential equation as the position of a very small body orbiting a body with a mass equal to the sum of the two masses, because

$\frac{m_1 m_2}{m_{red}} = m_1 + m_2,$

II. 1-Dimensional Quantum Harmonic Oscillator

With respect to describing the dynamics of atoms and molecules, the particle-in-a-box wavefunctions help us describe the quantum mechanical analogue of particle **translational motion**. Molecules can also have vibrational and rotational dynamics, both of which can be formulated and determined in a quantum mechanical framework.

Keep in mind: **quantization** will arise from **boundary conditions** when solving Schrodinger's Equation, as was discussed in the case of the particle-in-a-box.

Ia. Schrodinger Equation Solution for Harmonic Potential

We have seen from the particle in a box problem that the potential, $V(x)$, helps to define the nature of solutions to the time-independent Schrodinger equation. For a system characterized by the relative motion of two masses connected by a spring of force constant k, with small displacements from equilibrium, the potential can be taken as a harmonic (Hookean) form:

$$V(x) = \frac{1}{2}kx^2$$

This problem can be cast equivalently in terms of the motion of a relative mass defined as $\frac{m_1 m_2}{m_1 + m_2}$ (as done in Engel and Reid); here we will work with the absolute mass of a particle. To write the Schrodinger equation for the quantum harmonic oscillator, we consider the energy for the **classical total energy for a harmonic oscillator** derived above using the general solution.

In the classical sense:

$$E = T + V(x) = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}\,m\omega_0^2 x^2$$

We have seen that the quantum mechanical **operators** for the momentum and position are (Table , Engel and Reid) $x = \hat{X}$ and $p = \hat{P} = -\frac{i}{\hbar}\frac{d}{dx}$. Thus, the quantum analogue for the total energy is the Hamiltonian operator, which uses the momentum and position operators to represent the kinetic and potential energies of the quantum system as:

3

$$\hat{H} = \frac{1}{2m}\hat{P}^2 + \frac{1}{2}m\omega_0^2\hat{X}^2$$

The Hamiltonian, as in the classical case, is independent of time, and so we can solve the eigenvalue equation for the stationary states:

$$\hat{H}\psi(x) = E\psi(x)$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + \frac{1}{2}m\omega_0^2 x^2\psi(x) = E\psi(x)$$

If we define several alternate variables, the expression can be cast in a dimensionless form. This is important as we will see in a moment.

$$y = \frac{x}{\alpha} \quad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \quad \epsilon = \frac{2}{\hbar\omega_0}E$$

$$\frac{d^2\psi(x)}{dy^2} - y^2\psi(x) + E\psi(x) = 0$$

This is Hermite's associated differential equation. The solutions of this equation have been determined using a variety of methods (see Cohen-Tannoudji, Diu, and Laloe. *Quantum Mechanics*, Volume 1., Chap 5 and complements).

The eigenvalues of this Hamiltonian are:

$$\mathbf{E_n} = \left(\mathbf{n} + \frac{\mathbf{1}}{\mathbf{2}}\right)\mathbf{\hbar\omega_0} \qquad \mathbf{n = 0, 1, 2, 3, ...\infty}$$

Thus, for the q.m. harmonic oscillator, the energy is **quantized** and cannot take on arbitray values as in the classical case. Again, the ground state energy (as in the particle-in-a-box case) is non-zero, and equal to $\frac{\hbar\omega_0}{2}$.

IIb. Harmonic Oscillator Wavefunctions
The associated wavefunctions for the Hamiltonian are products of Gaussians and Hermite Polynomials. The Gaussian is the standard exponential in x^2 while the Hermite polynomials are a recursive set of *functions* possesing a

special type of symmetry. The Hermite polynomials possess either even or odd symmetry depending on the quantum number associated with them. For a full discussion of the derivation of these wavefunctions, see Cohen-Tannoudji *et al.*

The Hermite polynomials are an orthogonal set of functions. This is consistent since they are eigenfunctions of the total energy operator (Hamiltonian) for the harmonic oscillator. They arise as a result of assuming a **polynomial form for solutions to the Hermite differential equation**. Thus, each polynomial of degree n becomes a solution (and an eigenfunction) for the Hamiltonian.

Wavefunctions

$$\psi_n(x) = A_n H_n \left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{2\alpha^2}} \quad n = 0, 1, 2, 3, ..., \infty$$

$$\alpha = \left[\frac{\hbar^2}{km}\right]^{\frac{1}{4}}$$

$$\omega_0 = \sqrt{\frac{k}{m}} \quad (1)$$

Table Hermite Polymials

Quantum Number, n	$H_n(y) = H_n(\frac{x}{\alpha})$	Symmetry
0	1	Even
1	$2y$	Odd
2	$4y^2 - 2$	Even
3	$8y^3 - 12y$	Odd

General Recursion Relation: $H_{n+1}(y) = 2\ y\ H_n(y)\ -\ 2\ n\ H_{n-1}(y)$

Note
1. 1-D harmonic oscillator has equally spaced energy levels
2. Constant Energy spacing defined by fundamental frequency, ω_0. Contrast to P-I-B energy level spacing at high quantum numbers
3. Energy levels are non-degenerate: only 1 state per energy level
4. Wavefunctions are orthogonal set of polynomial functions known as Hermite Polynomials

5. Symmetry of wavefunctions alternates between even and odd based on quantum number

6. Finite probability of finding the quantum oscillator in classically forbidden regions (outside of classical turning points;tunneling)

7. Probability of finding a Particle in the Harmonic Oscillator Potential
Classical

particle is most likely to be found near the edges. particle is moving more quickly in the middle of the potential we'd expect the particle to spend less time in the middle because it is moving rapidly and more time at the edges were it is moving more slowly. the chance of finding the particle at a particular location is related to the amount of time spent there Thus, we have a better chance of finding the particle at the edges and less in the middle.

Quantum Mechanics

for the ground state of the system, the wave function has its maximum value in the middle of the potential, which means that the probability of finding the particle is highest in the center. as we look at higher energy states (increase n), the probability of finding the particle in the center decreases and the probability of finding the particle at the edges increases. this is consistent with the correspondence principle that says in the limit of large n, the quantum approach should agree with the classical approach.

The following figures show characteristic wavefunctions; probabilities can be found in Engel and Reid (Figure).

Representative Wavefunctions

n=0

n=1

n=5

n=20
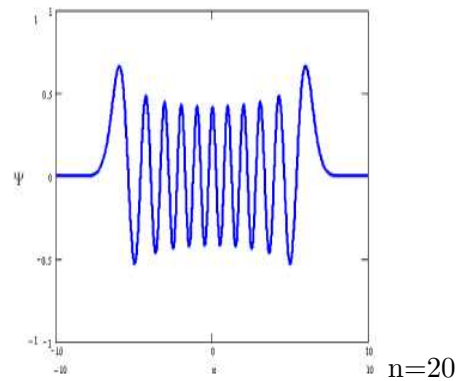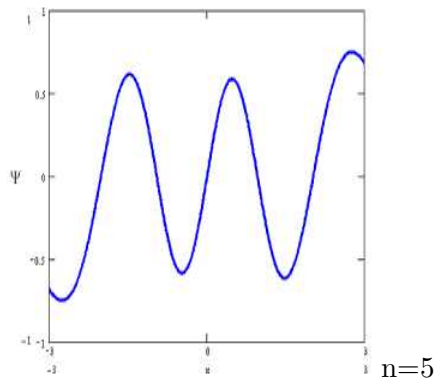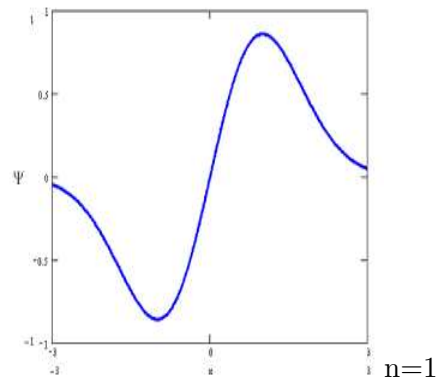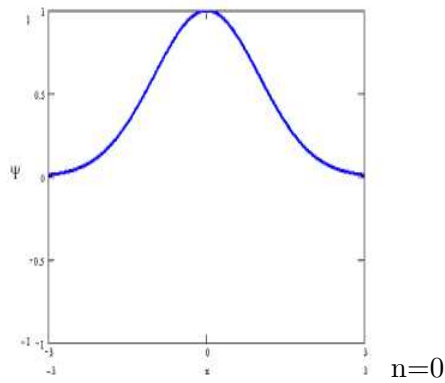
Symmetry Properties of Wavefunctions

$\Psi_{0,2,4,6,\ldots}$ are even functions. $\Psi(-x) = \Psi(x)$.

$\Psi_{1,3,5,7,\ldots}$ are odd functions. $\Psi(-x) = -\Psi(x)$.

Useful properties:
(even)(even) = even
(odd)(odd) = even
(odd)(even) = odd

$$\frac{d(odd)}{dx} = (even) \quad \frac{d(even)}{dx} = odd$$

$$\int_{-\infty}^{\infty} (odd)dx = 0 \quad \int_{-\infty}^{\infty} (even)dx = 2\int_{0}^{\infty} (even)dx$$

More detailed discussion of Hermite polynomial wavefunctions

7

Hermite Polynomials

A polynomial is a finite sum of terms like $a_k x_k$, where k is a positive integer or zero. There are sets of polynomials such that the product of any two different ones, multiplied by a function w(x) called a weight function and integrated over a certain interval, vanishes. Such a set is called a set of orthogonal polynomials. Among other things, this makes it possible to expand an arbitrary function f(x) as a sum of the polynomials, each multiplied by a coefficient c(k), which is easily and uniquely determined by integration. A Fourier series is similar, but the orthogonal functions are not polynomials. These functions can also be used to specify basis states in quantum mechanics, which must be orthogonal.

The Hermite polynomials $H_n(x)$ are orthogonal on the interval from $-\infty$ to $+\infty$ with respect to the weight function $w(x) = e^{x^2}$. Surprisingly, this is sufficient to determine the polynomials up to a multiplicative factor. Let's start with the expression $H_n = e^{x^2}(d^n/dx^n)e^{-x^2}$. We notice that each differentiation will bring down a factor $-2x$, and that the exponential will survive in each term. Each term will contain the factor $exp(-x^2)$ that will be cancelled by the exponential in front. Therefore, the result will be a polynomial of degree n, and the leading term will be $(-2x)^n$. The powers of x will either be all even or all odd, as well. Moreover, the form of this definition will guarantee that the polynomials belonging to different values of n are orthogonal.

An alternative definition uses the weight function $w(x) = e^{x^2/2}$ instead. Then, $He_n = e^{x^2/2}(dn/dx^n)e^{-x^2/2}$, where the notation He is used instead of H to make the different weight function clear. Of course, the corresponding polynomials will be very similar, and one could be used as well as the other, with appropriate changes of variable. In this case, each differentiation brings down the simpler factor $(-x)$, so that the coefficient of x^n is $(-1)^n$. In fact, the usual definitions include the $(-1)^n$ factor, so that the coefficient of x^n is always positive. Of three classic references (see References), Jackson uses He, Pauling and Wilson H, and both are given in Abramowitz and Stegun. The possibilities of confusion are not as great as in the case of Laguerre polynomials.