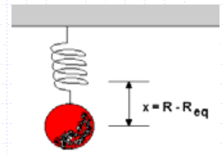
Physical Chemistry

Lecture 14

The 1-D Harmonic Oscillator

The 1-D harmonic oscillator hamiltonian

- Particle (mass m) attached to a spring of force constant, k



- Potential energy depends on position as a Hooke's-law spring

$$V = \frac{k}{2}(r - r_{eq})^2 = \frac{k}{2}x^2$$

$$H = \frac{p^2}{2m} + \frac{k}{2}x^2$$

Classical solution of the 1-D harmonic oscillator

- Solve for trajectories for constant energy
- Fundamental frequency, ω_0
- Oscillatory motion
- Maximum displacements are classical turning points
  - E = V(x_{max})

$$x(t) = \sqrt{\frac{2E}{m\omega_0^2}}\cos\omega_0 t$$

$$p(t) = -\sqrt{2mE}\sin\omega_0 t$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

$$x_{\max} = \pm\sqrt{\frac{2E}{m\omega_0^2}}$$

Quantum 1-D harmonic oscillator

- **Schroedinger's equation**

$$H\Psi = E\Psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \frac{k}{2}x^2\Psi = E\Psi$$

- **Convenient to make dimensionless equation**

$$\frac{d^2\Psi}{dy^2} - y^2\Psi + \varepsilon\Psi = 0$$

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

- **Hermite's associated differential equation**

1-D harmonic-oscillator wave functions and energies

- Wavefunctions

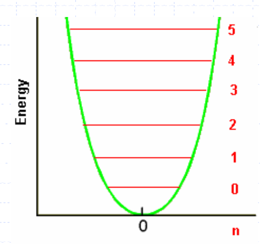
$$\Psi_\upsilon(x) = A_\upsilon H_\upsilon(x/\alpha)\exp\left(-\frac{x^2}{2\alpha^2}\right) \qquad \upsilon = 0, 1, 2, 3, \ldots$$

- Energy eigenvalues

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)\hbar\omega_0 = \left(\upsilon + \frac{1}{2}\right)h\nu_0$$

Energy levels

- The 1-D harmonic oscillator has equally spaced energy states
- Energy spacing depends on the fundamental frequency
- Energy levels are nondegenerate
  - One state per level



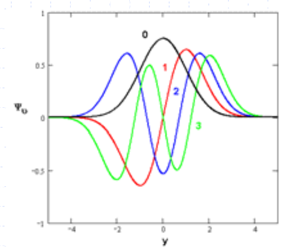
Harmonic-oscillator wave functions

- Harmonic-oscillator wave functions are related to the Hermite polynomials
- Hermite polynomials are well-known sets of functions

υ	$H_\upsilon(y)$	Symmetry
0	1	Even
1	$2y$	Odd
2	$4y^2 - 2$	Even
3	$8y^3 - 12y$	Odd

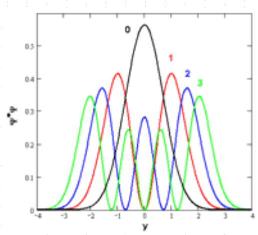
Wave functions

- Hermite polynomials multiplied by a Gaussian function
- Note alternation in symmetry about x = 0
  - Even
  - Odd



Probability Functions

- The square of the wave function gives the probability density at each position
- Finite possibility the particle is outside of the classical turning points



Summary

- Harmonic oscillator is easily identified as
  - Hermite's differential equation
- Nondegenerate levels
- Symmetry about x = 0 alternates with quantum number
- Equally spaced energy levels
- Finite probability of finding the particle in the classically forbidden region (where the potential energy is greater than the total energy)