Lecture 15, Feb 13, 2023

Absorption of Photons

- The probability of absorption of a photon by a molecule depends on the dipole strength $D_{0A} = \|\vec{\mu}_{0A}\|^2$ where 0 is the ground state and A is the excited singlet state
- Beer's law: $\frac{I(\lambda)}{I_0(\lambda)} = e^{-\varepsilon(\lambda)Cb}$
  - Exponential decay of transmitted light intensity
  - C is the amount of material (concentration)
  - b is the path length
  - ε is the molar absorptivity (absorption strength)

Vibrational Energies

- Harmonic oscillator is a very good approximation for the potential
- The true potential is the Morse potential
- Molecules have dipole moments, which allows absorption of electromagnetic radiation
  - $\frac{\mathrm{d}\mu}{\mathrm{d}r} > 0$, i.e. the electric dipole must change with bond length during a vibration
  - This is why oxygen and nitrogen gas don't cause climate change but water vapour does
    * Carbon dioxide is normally linear, but when it vibrates there is a dipole
  - Vibrational energies are close together so the transitions are infrared
- Due to the deviation between the real potential and the harmonic oscillator, this gives it antiharmonic character which allows energy redistribution
- Example: water
  - 3 normal modes of vibrations (9 DoF from each atom - 3 translation - 3 rotation, to put it in molecular frame)
  - all 3 have dipole moments, so they are all IR active, making it a very good infrared absorber
- Quantum harmonic oscillator: $U = \frac{1}{2}kx^2$
  - Boundary conditions: symmetry, and approaches zero for $x \to \infty$
  - Solution has energies given by $E = \frac{1}{2}(n+1)h\nu$
  - This has a zero point energy of $\frac{1}{2}h\nu$ – even at 0 kelvin, atoms are still moving
    * This is due to the uncertainty relation
  - Energies are equally spaced, unlike the particle in a box
  - The actual wavefunctions are given by $\psi_n(x) = N_n e^{-\beta^2 x^2/2} H_n(\beta x)$, where n is an integer quantum number, $\beta = \sqrt{\frac{mv}{h}}$, and H_n are the *Hermite polynomials*

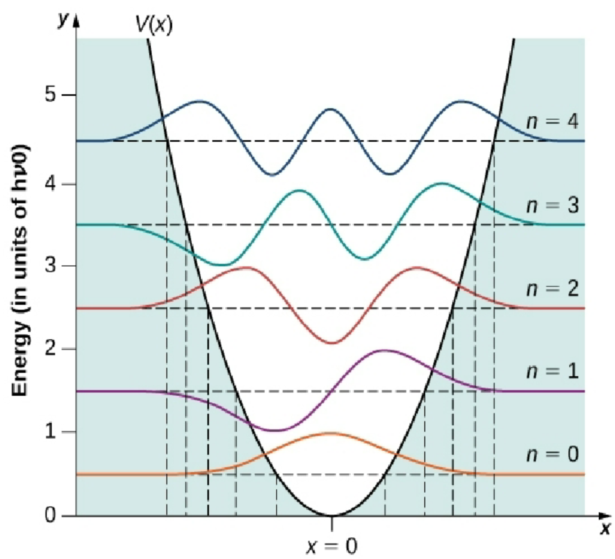

Figure 1: Shapes and energies of the quantum harmonic oscillator solutions