Lecture 18:
Intro. to Quantum Mechanics

• Reading: Zumdahl 12.5, 12.6

• Outline
  – Basic concepts of quantum mechanics and molecular structure
  – A model system: particle in a box.
  – Other confining potentials.
Quantum Concepts

• The Bohr model was capable of describing the discrete or “quantized” emission spectrum of H.

• But the failure of the model for multielectron systems combined with other issues (the ultraviolet catastrophe, workfunctions of metals, etc.) suggested that a new description of atomic matter was needed.
Wave-Particle Duality

- This new description is known as wave mechanics or quantum mechanics.
- Recall, photons and electrons readily demonstrate wave-particle duality.
- The idea behind wave mechanics is that the existence of the electron in fixed energy levels should be though of as a “standing wave”, rather than a particle’s trajectory.
- Think about two ways to describe your travels during the day, one uses position and time (the classical way), and the other is just position and probability (the statistical description).
- Q.M. Provides a way to describe an electron probabilistically without saying in detail how it moves from place to place (that idea must be discarded).
Q.M. Concepts

• What is a standing wave?

- A standing wave is a motion in which translation of the wave does not occur.

- In the guitar string analogy (illustrated), note that standing waves involve nodes in which no motion of the string occurs.

- Note also that integer and half-integer values of the wavelength correspond to standing waves.
Q.M.: deBroglie Relation

- Louis de Broglie suggests that for the $e^-$ orbits envisioned by Bohr, only certain orbits are allowed since they satisfy the standing wave condition.

\[ h = p\lambda \]
Q.M.: Operators

- Erwin Schrödinger develops a mathematical formalism that incorporates the wave nature of matter:

\[ \hat{H} \psi = E \psi \]

The Wave Equation:

The Hamiltonian:

\[ \hat{H} = \frac{\hat{p}^2}{2m} + (PE) \]

The Wavefunction: \( \psi \) is a solution to the wave equation problem

E = energy; also found when solved
Q.M.: Wavefunctions

• What is a wavefunction?

\[ \psi = \text{a probability amplitude} \]

• Consider a wave:

\[ y = Ae^{i((2\pi\nu)t+\varphi)} = A \left\{ \cos \left( (2\pi\nu)t + \varphi \right) + i \sin \left( (2\pi\nu)t + \varphi \right) \right\} \]

Intensity = \[ |y|^2 = \left( Ae^{i((2\pi\nu)t+\varphi)} \right) \left( Ae^{-i((2\pi\nu)t+\varphi)} \right) = A^2 \]

• Probability of finding a particle in space:

\[ \text{Probability} = \psi^* \psi \]

• With the wavefunction, we can describe spatial distributions.
QM: Uncertainty

- Another error of the Bohr model was that it assumed we could know both the position and momentum of an electron exactly.

- Werner Heisenberg’s development of quantum mechanics leads to the understanding that there is a fundamental limit to how well one can know both the position and momentum of a particle.

\[ \Delta x \cdot \Delta p \geq \frac{1}{2} \hbar = \frac{1}{2} \frac{h}{2\pi} \]

Uncertainty in position Uncertainty in momentum, which is mass times velocity
Uncertainty

• Example: What is the uncertainty in velocity for an electron in a 1Å radius orbital in which the positional uncertainty is 1% of the radius.

\[ \Delta x = (1 \text{ Å})(0.01) = 1 \times 10^{-12} \text{ m} \]

\[ \Delta p = \frac{h}{4\pi\Delta x} = \frac{(6.626\times10^{-34} \text{ J.s})}{4\pi(1\times10^{-12} \text{ m})} = 5.27\times10^{-23} \text{ kg.m/s} \]

\[ \Delta v = \frac{\Delta p}{m} = \frac{5.27\times10^{-23} \text{ kg.m/s}}{9.11\times10^{-31} \text{ kg}} = 5.7\times10^7 \text{ m/s} \]

So we really have to give up the idea we know (even roughly) the position and velocity at the same time.
Uncertainty

- Example (you’re quantum as well):

What is the uncertainty in position for a 80 kg student walking across campus at 1.3 m/s with an uncertainty in velocity of 1%.

\[ \Delta p = m \Delta v = (80 \text{ kg})(0.013 \text{ m/s}) = 1.04 \text{ kg.m/s} \]

\[ \Delta x = \frac{h}{4\pi\Delta p} = \frac{\left(6.626 \times 10^{-34} \text{ J.s}\right)}{4\pi(1.04 \text{ kg.m/s})} = 5.07 \times 10^{-35} \text{ m} \]

Very small……we know where you are.
Potentials and Quantization

• Consider a particle free to move in 1 dimension:

  \[ \psi(p) = \frac{1}{2m} \psi(p) = \frac{1}{2} mv^2 \psi(p) = E \psi(p) \]

  “The Free Particle”

  Potential E = 0

• The Schrodinger Eq. becomes:

  \[ \hat{H} \psi = \left( \frac{\hat{p}^2}{2m} + PE \right) \psi(p) = \frac{\hat{p}^2}{2m} \psi(p) = E \psi(p) \]

  Energy ranges from 0 to infinity…not quantized.
Particle (electron) in a box or trap

- What if the position of the particle is constrained by a potential:

  “Particle in a Box”

  Potential $E$

  $= 0$ for $0 \leq x \leq L$

  $= \infty$ all other $x$

- Now, position of particle is limited to the dimension of the box.
Particle in a Box: Potential
What do the wavefunctions look like?

\[ \Psi(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right) \]

\[ n = 1, 2, 3 \ldots \]

A standing wave: \( n \) is an integer counter, that keeps track of the different energies.
Energy is quantized

\[ E = \frac{n^2 \hbar^2}{8mL^2} \]

\( n = 1, 2, \ldots \)
Optical Spectra using P.in B.

- Consider the following dye molecule, the length of which can be considered the length of the “box” an electron is limited to:

\[
\Delta E = \frac{\hbar^2}{8mL^2} \left( n_{\text{final}}^2 - n_{\text{initial}}^2 \right) = \frac{\hbar^2}{8m(8\text{Å})^2} \left( 2^2 - 1 \right) = 2.8 \times 10^{-19} \text{ J}
\]

\[
\lambda \approx 700 \text{ nm}
\]

(should be 680 nm)
Potentials and Quantization (cont.)

• One effect of a “constraining potential” is that the energy of the system becomes quantized.

• Back to the hydrogen-like atom:

\[ V(r) = \frac{-e^2}{r} Z \]
• Also in the case of the hydrogen atom, energy becomes quantized due to the presence of a constraining potential.

Above zero (positive energy states) the energy is not quantized; any K.E. is O.K. Recovers the “Bohr” behavior.