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CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 17: Introduction to Molecular Structure

References

1. Levine, *Physical Chemistry*, 19.1–19.3

Key Concepts

- Our general strategy to understand molecular structure will be similar to the approach we took for atomic structure:
  1. Identify the system of interest: in this case multiple electrons and nuclei
  2. Write the potential energy (V): this will be complex since there are electron-electron, electron-nucleus, and nucleus-nucleus interactions
  3. Solve the Schrödinger Equation : $\hat{H}\Psi = E\Psi$, this is hard since $\hat{H}$ contains all the cross terms for the interactions noted above
  4. Find $\{\Psi, E\}$: use Ψ to determine E, structure $\leftrightarrow$ energies $\leftrightarrow$ properties
- To make this problem tractable, we need to separate the different contributions to the total energy. The ones that will of most interest to us are:
  1. Electronic: chemical bonding in molecules will depend on what the electrons are doing & their energies (UV/Vis)
  2. Vibrations: how bonds are bending and stretching (IR)
  3. Rotations: how molecules rotate and the associated rotational energy states (microwave)
  4. Nuclear: even though they are heavy they have an associate energy of motion (radio, NMR)

  The term in parentheses indicate the part of the spectrum that corresponds to the associated energy type listed above. In this light, it makes physical sense to separate them since their relative energies differ by several orders of magnitude.
- To investigate the electronic energies of a molecule we need to make a further approximation, namely the Born-Oppenheimer approximation. This states that since the electrons are several orders of magnitude lighter than the nuclei, we can consider the nuclei to be separated by a fixed distance R.
- This results in the following general procedure for approaching molecular structure:
  1. Fix the distance between the nuclei at R
  2. Find the resulting Ψ's and associated electronic energies, E_{elc}
  3. Now vary R and determine the electronic energy as a function of R, $E(R)$,
  4. Minimize $E(R)$ to find physical quantities such as the bond length and energy ($\frac{dE}{dR} = 0$)
- The simplest molecule to consider is the one-electron molecule, H_2^+. We'll tackle the solutions to this problem next time.