Physical Chemistry

Lecture 22
Diatom Molecules

Geometry of dihydrogen
- Dihydrogen
  - Two nuclear centers
  - Two electrons
- Focus on translation and Coulombic interactions
  - Nuclear translation
  - Electronic translation
  - Nuclear repulsion
  - Nuclear-electron attraction
  - Electron-electron repulsion
  - Spin-orbit coupling

\[ \hat{H} = \hat{T} + \hat{V}_n + \hat{V}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{H}_{so} \]

Center of mass
- Treat the system as if electrons were massless for purposes of determining the center of mass
  - \( m_e = m_p/1836 \)
  - Good approximation
- Center of mass determined by the positions of the nuclei
- Center-of-mass problem is again a particle in a box

Relative problem
- Nuclei and electrons move relative to the center of mass
- Cannot readily use prior techniques to separate electron and nuclear motions because of the Coulomb potentials

Born-Oppenheimer approximation
- Solve problem in steps
- Consider nuclei fixed and find electronic wave function at each nuclear configuration
- Electronic wave functions found this way depend on position of nuclei
- Subsequently, use electronic wave functions to solve for the nuclear motion in an apparent internuclear potential, \( E(R) \)
- Works because electrons move much faster than the nuclei

Solving the nuclear problem approximately
- Manipulation of Schroedinger’s equation gives an equation for the nuclear motion
  \[ \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} J^2 + E(R) \Psi_n = E\Psi_n \]
- Solution is factorable into a function of the internuclear distance, \( R \), and the spherical harmonic functions
  \[ \Psi_n = \zeta(R) Y_{\ell m}(\theta, \phi) \]
- To solve \( R \) portion, one must know \( E(R) \) explicitly
Harmonic approximation

- Must determine $E(R)$ to solve equation
- Use expansion about $R_0$
- Truncate at first term, which gives harmonic approximation
- Gives a harmonic-oscillator form for the movement of the nuclear
- Correct by adding perturbation energies for higher-order terms

$$E(R) = E(R_0) + \frac{1}{2} \left( \frac{\partial^2 E}{\partial R^2} \right)_R (R-R_0)^2 + \ldots$$

Vibrational energies

- Solution of relative nuclear movement is like a harmonic oscillator
- Quantum numbers $n = 0, 1, 2, 3, \ldots$
- Corrections to account for difference between harmonic potential and real internuclear potential of anharmonic oscillator

$$E_{\text{vib}} = \left( n + \frac{1}{2} \right)^2 \hbar \nu_v - \left( n + \frac{1}{2} \right) \hbar \nu_v + \ldots$$

Rotational energies

- Treat like an approximate rigid rotor
- Energy depends on $J$
- Equilibrium rotational constant, $B_e$
- Vibrational state affects $B_e$
- Centrifugal distortion adds another term

$$E_{\text{rot}} = B_e \hbar J(J+1) - D_e J^2 (J+1)^2$$

Overall diatomic energy

- Vibrational and rotational states slightly affect each other
- Add small terms by perturbation theory
  - Vibration-rotation coupling
  - Centrifugal distortion
- Include electronic energy at equilibrium, called $-D_e$

$$E_{\text{total}} = -D_e + \left( n + \frac{1}{2} \right)^2 \hbar \nu_v - \left( n + \frac{1}{2} \right) \hbar \nu_v + \ldots$$

Spectroscopy of a diatomic molecule

- Absorption of electromagnetic radiation by transitions between states
  - Absorption
  - Emission
  - Simultaneous change of several energies

Spectroscopy of a diatomic molecule

- Vibrational-rotational spectroscopy
- Selection rules
  - $\Delta J = \pm 1$
  - $\Delta n = \pm 1$
- Infrared region
### Spectroscopy of a diatomic molecule

- Vibration-rotation spectroscopy in the infrared region
- Requires the molecule to have a dipole moment
- Most molecules in ground vibrational state at room conditions
  - Vibrational transitions from the ground state only
  - At higher temperatures, transitions from higher-energy vibrational states – **not bands**

### Summary

- Can put the hydrogen-molecule problem in the form of model problems
- Correct for discrepancies between the real coupling and the model problems
  - Use perturbation theory
- Have a form for the energy of a diatomic molecule that consists of terms
  - Depends on vibrational and rotational quantum numbers
  - Can predict spectra of diatomic molecules from this form
- Did not specifically solve for electronic states
  - Form of electronic states is important in determining E(R)