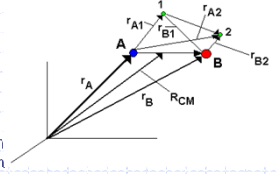


Physical Chemistry

Lecture 22
Diatomic 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



$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} + \hat{H}_{SO}$$

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

$$\hat{T}_n = -\frac{\hbar^2}{2\mu} \nabla_n^2$$

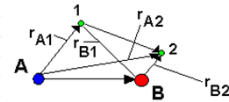
$$\hat{T}_{CM} = -\frac{\hbar^2}{2M} \nabla_{CM}^2$$

$$M = m_A + m_B$$

$$\mu = \frac{m_A m_B}{M}$$

Relative problem

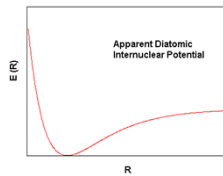
- ◆ Nuclei and electrons move relative to the center of mass
- ◆ Cannot readily use prior techniques to separate electron and nuclear motions because of the Coulomb potentials



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, R
- ◆ Subsequently, use electronic wave functions to solve for the motion of the nuclei in an apparent internuclear potential, E(R)
- ◆ Works because electrons move much faster than the nuclei

$$\Psi \equiv \Psi_n(r_n, \theta_n, \phi_n) \Psi_e(\mathbf{R}, \mathbf{r}_e)$$



Solving the nuclear problem approximately

- ◆ Manipulation of Schrodinger's equation gives an equation for the nuclear motion

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} J^2 + E(R) \right] \Psi_n = E \Psi_n$$

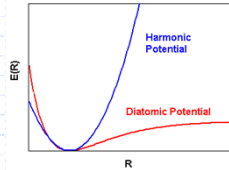
- ◆ Solution is factorable into a function of the internuclear distance, R, and the spherical harmonic functions

$$\Psi_n = \zeta(R) Y_{lm}(\theta_n, \phi_n)$$

- ◆ To solve R portion, one must know E(R) explicitly

Harmonic approximation

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



$$E(R) = E(R_e) + \frac{1}{2!} \left(\frac{\partial^2 E}{\partial R^2} \right)_{R_e} (R - R_e)^2 + \frac{1}{3!} \left(\frac{\partial^3 E}{\partial R^3} \right)_{R_e} (R - R_e)^3 + \dots$$

Vibrational energies

- ◆ Solution of relative nuclear movement is like a harmonic oscillator
 - Use a quantum number $n = 0, 1, 2, 3, \dots$
- ◆ Corrections to account for difference between harmonic potential and real internuclear potential of anharmonic oscillator

$$E_{vib} = \left(n + \frac{1}{2} \right) h \nu_0 - \left(n + \frac{1}{2} \right)^2 x_e h \nu_0 + \dots$$

Rotational energies

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

$$E_{rot}^{(0)} = B_e h J(J+1)$$

$$B_e = \frac{\hbar}{4\pi\mu R_e^2}$$

$$B_n = B_e - \alpha_e \left(n + \frac{1}{2} \right)$$

$$- D_c J^2 (J+1)^2$$

$$E_{rot} = B_n J(J+1) - D_c J^2 (J+1)^2$$

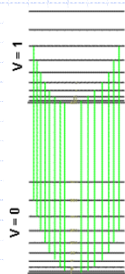
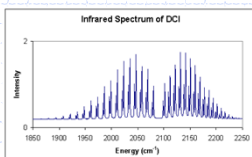
Overall diatomic energy

- ◆ 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 $-D_e$

$$E_{n,J} = -D_e + \left(n + \frac{1}{2} \right) h \nu_0 - \left(n + \frac{1}{2} \right)^2 x_e h \nu_0 + \dots + \left(B_e + \alpha_e \left(n + \frac{1}{2} \right) \right) J(J+1) - D_c J^2 (J+1)^2$$

Spectroscopy of a diatomic molecule

- ◆ Vibrational-rotational spectroscopy
- ◆ Selection rules
 - $\Delta J = \pm 1$
 - $\Delta n = \pm 1$
- ◆ Infrared region



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 $E(R)$