CBE 310 Molecular Concepts and Applications

Spectroscopy

10 01 2014

Helium and Hydrogen molecular ion
The Variational Method

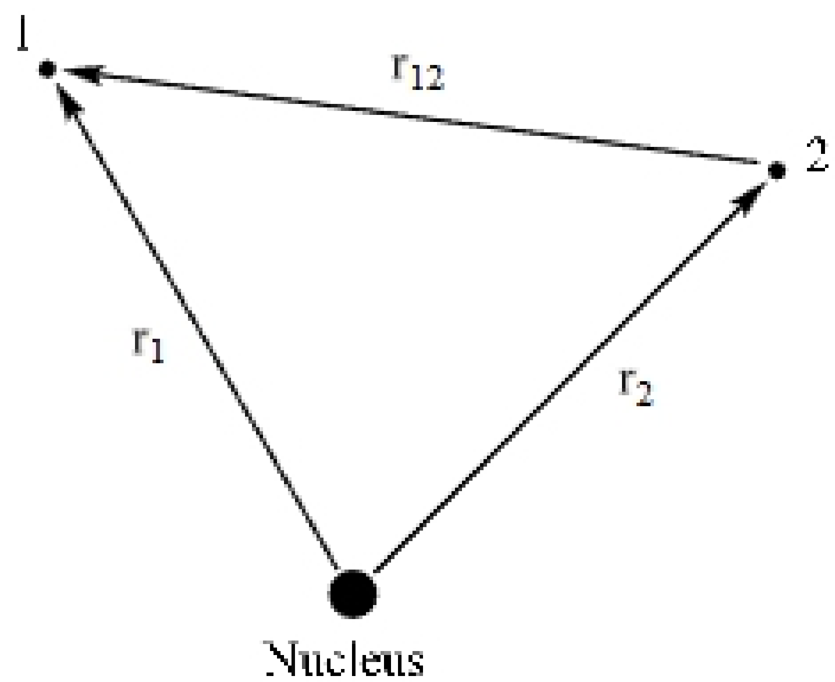
An expansion on the idea of light interacting with matter
A second basis for selection rules
Calculating the transition state dipole moment
Stimulated absorption and emission
Spectroscopy

Hamiltonian for Helium

$$H(1,2,3....n) = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Z}{r_i} + \frac{1}{2}\sum_{i\neq j}^{n}\frac{1}{r_{ij}}$$

For helium this becomes

$$H(1,2) = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$



$$H(1,2) = h(1) + h(2) + \frac{1}{r_{12}}$$

Here we get stuck

$$h(i) = -\frac{1}{2}\nabla_i^2 - \frac{2}{r_i}$$

1 electron Hamiltonian for electron #1)

Hamiltonian for Helium

$$H(1,2) = h(1) + h(2) + \frac{1}{r_{12}}$$

$$h(i) = -\frac{1}{2}\nabla_i^2 - \frac{2}{r_i}$$

Here we get stuck because we can not separate the electron repulsion terms

$$H_{approx} = h(1) + h(2)$$

The small h Hamiltonians are the solutions to the hydrogen atoms

$$\phi_1 = 1s \qquad h(1)\phi_i(1) = \varepsilon_i \phi_i(1)$$

$$\phi_2 = 2s$$

$$\phi_3 = 2p_x$$

The small ϕ are the solutions to the hydrogen atoms, the various orbitals