

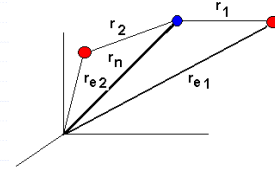
# Physical Chemistry

## Lecture 17

### The Helium Atom's Spatial States

## The helium atom

- Consists of a nucleus and two electrons
- Hamiltonian has four kinds of terms
  - Nuclear kinetic energy
  - Electronic kinetic energy
  - Nuclear-electron Coulombic potential energy
  - Electron-electron Coulombic potential energy



$$H = T_n + T_{e1} + T_{e2} + V_{ne1} + V_{ne2} + V_{ee}$$

$$= \frac{p_n^2}{2m_n} + \frac{p_{e1}^2}{2m_e} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0} \left( \frac{1}{|r_1|} + \frac{1}{|r_2|} \right) + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

## Center of mass separation

- Focus on the relative problem
- Center of mass is assumed to be at the nucleus
  - Good approximation as nuclei get heavier
  - Determine only relative energies of a single atom
  - Center-of-mass problem again gives a particle-in-a-box solution; translational energies

$$H = T_{e1} + T_{e2} + V_{ne1} + V_{ne2} + V_{ee}$$

$$= \frac{p_{e1}^2}{2m_e} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0} \left( \frac{1}{|r_1|} + \frac{1}{|r_2|} \right) + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

## Simplification of the helium-atom problem

- Consider the problem with neglect of the electron-electron repulsion

$$H = T_{e1} + V_{ne1} + T_{e2} + V_{ne2}$$

$$= \frac{p_{e1}^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{|r_1|} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0} \frac{1}{|r_2|}$$

- Decompose into two hydrogen-like problems

$$H_1 \Psi_1(\mathbf{r}_1) = E_1 \Psi_1(\mathbf{r}_1) \quad H_2 \Psi_2(\mathbf{r}_2) = E_2 \Psi_2(\mathbf{r}_2)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2) \quad E = E_1 + E_2$$

## Hydrogen-like energies and wave functions

- Difference between the approximate helium atom and the hydrogen atom
  - Z = 1 for hydrogen
  - Z = 2 for helium
- Nuclear-charge difference produces scaling of wave functions and energies
- Each electron of helium is defined by three quantum numbers, but the energy depends on only the principal quantum number

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(Zr/a_0) Y_{lm}(\theta, \phi)$$

$$E_n = -\frac{Z^2 E_h}{2} \frac{1}{n^2}$$

## Approximate wave functions and energies for helium

- In the simplest approximation, wave functions are products of one-electron wave functions
- Energies are sums of one-electron energies

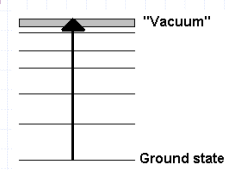
$$\Psi_{n_1, l_1, m_1, n_2, l_2, m_2}(\mathbf{r}_1, \mathbf{r}_2) \psi_{spin} = \Psi_{n_1, l_1, m_1}(\mathbf{r}_1) \Psi_{n_2, l_2, m_2}(\mathbf{r}_2) \psi_{spin}$$

$$E_{n_1, l_1, m_1, n_2, l_2, m_2} = -\frac{Z^2 E_h}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

## Independent-electron energies of the helium atom

- ◆ Consider the state with lowest energy  $E_{1,1} = -\frac{2^2 E_h}{2} \left( \frac{1}{1^2} + \frac{1}{1^2} \right)$
  - ◆ Each electron has a principal quantum number of 1
    - $n_1 = 1$
    - $n_2 = 1$
  - ◆ Next highest
    - $n_1 = 1$  and  $n_2 = 2$
    - $n_1 = 2$  and  $n_2 = 1$
- $$E_{1,1} = -\frac{2^2 E_h}{2} \left( \frac{1}{1^2} + \frac{1}{1^2} \right) = -4 E_h = -108.8 eV$$
- $$E_{1,2} = -\frac{2^2 E_h}{2} \left( \frac{1}{1^2} + \frac{1}{2^2} \right) = -\frac{5}{2} E_h = -68.0 eV$$

## Checking energies – the ionization potential

- ◆ We measure energy differences
  - ◆ Consider the ionization process
  - ◆ The energy change of this process can be measured with a mass-spectrometric experiment
  - ◆ Experimental first ionization potential of helium is **24.6 eV**
  - ◆ First ionization potential theoretically predicted to be much larger by this independent-electron approximation
    - Must reconsider the approximation
- 
- "Vacuum"  
Ground state
- $$He \rightarrow He^+ + e^-$$
- $$\Delta E = E_{1s, He} - E_{(1s)^2, He} = -54.4 eV - (-108.8 eV) = 54.4 eV$$

## Problems with independent-electron approximation

- ◆ Neglect of **electron-electron repulsion** gives an incomplete picture of the energy situation
  - Major source of error
  - Model does not represent the situation accurately
- ◆ Must incorporate electron-electron repulsion to give a "better" picture of the energy state
- ◆ Can be done by several procedures
  - Exact calculation – **very hard**
  - Perturbation theory
  - Variational calculation

## Perturbation theory

- ◆ With an approximate wave function, one can calculate an approximate energy
    - Use independent-electron product wave functions
  - ◆ The Hamiltonian must include all terms
    - $H = H_a + H_b + V_{ee}$
    - $V_{ee}$  neglected in the independent-electron calculation
  - ◆ **First-order perturbation theory**
- $$E = \int_{all\ space} \Psi^*(\mathbf{r}) H \Psi(\mathbf{r}) d^3\mathbf{r}$$
- $$E_{ab} = \int_{all\ space} \Psi_a^*(\mathbf{r}_1) \Psi_b^*(\mathbf{r}_2) H_a \Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) d^3\mathbf{r} + \int_{all\ space} \Psi_a^*(\mathbf{r}_1) \Psi_b^*(\mathbf{r}_2) H_b \Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) d^3\mathbf{r} + \int_{all\ space} \Psi_a^*(\mathbf{r}_1) \Psi_b^*(\mathbf{r}_2) V_{ee} \Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) d^3\mathbf{r} = E_a^{(0)} + E_b^{(0)} + E^{(1)}$$

## Ground-state energy of helium through first order

- ◆ Coulomb repulsion integral, J
    - Average over a known wave function of the Coulombic interaction
    - Can be calculated through tedious calculus
    - Depends on the kinds of states involved
  - ◆ Total energy is a sum of the unperturbed energy with the first-order correction
- $$J_{1s,1s} = \int_{all\ space} \Psi_{1s}^*(\mathbf{r}_1) \Psi_{1s}(\mathbf{r}_1) \left( \frac{1}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi_{1s}^*(\mathbf{r}_2) \Psi_{1s}(\mathbf{r}_2) d^3\mathbf{r} = \frac{5}{4} E_h$$
- $$E = -4 E_h + \frac{5}{4} E_h = -\frac{11}{4} E_h = -74.8 eV$$

## Ionization potential with the Coulomb repulsion included

- ◆ The ionization potential is the measurement of the energy difference  $He \rightarrow He^+ + e^-$
  - ◆ With the inclusion of the electron repulsion, the ionization potential is much closer to the measured value
- $$\Delta E = E_{He,1s} - E_{He,(1s)^2} = -54.4 eV - (-74.8 eV) = 20.4 eV$$
- $$\Delta E_{exp} = 24.6 eV$$

## Variational principle

- ◆ One can guess any approximate wave function

- Use to calculate an approximate energy
- Approximate will be always be incorrect unless the true wave function is chosen

- ◆ **Variational principle**

- All approximate energies will be higher than the exact energy
- Can use this to "improve" the wave function and the energy

$$E_{app} = \int_{all\ space} \Psi_{app}^* H \Psi d^3\mathbf{r}$$

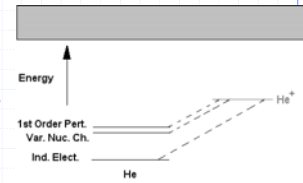
$$E_{app} \geq E_{true}$$

$$\frac{\partial E_{app}}{\partial c} = 0$$

## The approximations to the helium-atom energies

- ◆ The improvements of the wave function give improvements of the energies

- ◆ With modern computer-assisted techniques, one gets approximate states that are extremely close to the exact solution of the problem



## Summary

- ◆ One cannot solve for the helium atom's spatial states exactly
- ◆ Use first-order perturbation theory
  - Independent-electron model is solvable
  - "Correct" the energy by integral over unperturbed states
    - Evaluate Coulomb integrals
- ◆ Still not adequate to model the experimental data
  - Variational calculation allows a closer approach
  - Major problem is "correlation energy"
    - Electron avoidance
    - More sophisticated numerical solutions allow close approach to ground-state wave functions
      - Self-consistent field
      - Configuration interaction