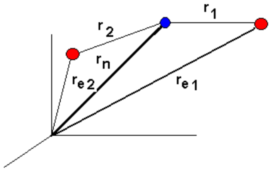
Physical Chemistry

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



$$H = T_n + T_{e1} + T_{e2} + V_{ne_1} + V_{ne_2} + V_{ee}$$
$$= \frac{p_n^2}{2m_n} + \frac{p_{e1}^2}{2m_e} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\mathbf{r}_1|}+\frac{1}{|\mathbf{r}_2|}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

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

$$H = T_{e1} + T_{e2} + V_{ne_1} + V_{ne_2} + V_{ee}$$
$$= \frac{p_{e1}^2}{2m_e} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\mathbf{r}_1|}+\frac{1}{|\mathbf{r}_2|}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Simplification of the helium-atom problem

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

$$H = T_{e1} + V_{ne_1} + T_{e2} + V_{ne_2}$$
$$= \frac{p_{e1}^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_1|} + \frac{p_{e2}^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_2|}$$

- Decompose into two hydrogen-like problems

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

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

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

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

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

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

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

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

Independent-electron energies of the helium atom

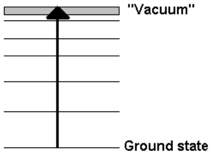
- Consider the state with lowest energy
- Each electron has a principal quantum number of 1
  - $n_1 = 1$
  - $n_2 = 1$
- Next highest
  - $n_1 = 1$ and $n_2 = 2$
  - $n_1 = 2$ and $n_1 = 1$

$$\begin{aligned} E_{1,1} &= -\frac{2^2 E_h}{2}\left(\frac{1}{1^2}+\frac{1}{1^2}\right) \\ &= -4\,E_h \\ &= -108.8\,eV \end{aligned}$$

$$\begin{aligned} E_{1,2} &= -\frac{2^2 E_h}{2}\left(\frac{1}{1^2}+\frac{1}{2^2}\right) \\ &= -\frac{5}{2}E_h \\ &= -68.0\,eV \end{aligned}$$

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



$$He \rightarrow He^+ + e^-$$

$$\begin{aligned} \Delta E &= E_{1s,He} - E_{(1s)^2,He} \\ &= -54.4\,eV - (-108.8\,eV) \\ &= 54.4\,eV \end{aligned}$$

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

$$E = \int_{\substack{all\\space}} \Psi^*(\mathbf{r}) H \Psi(\mathbf{r})\, d^3\mathbf{r}$$

$$\begin{aligned} E_{ab} &= \int_{\substack{all\\space}} \Psi_a^*(\mathbf{r}_1)\Psi_b^*(\mathbf{r}_2) H_a \Psi_a(\mathbf{r}_1)\Psi_b(\mathbf{r}_2)\, d^3\mathbf{r} \\ &+ \int_{\substack{all\\space}} \Psi_a^*(\mathbf{r}_1)\Psi_b^*(\mathbf{r}_2) H_b \Psi_a(\mathbf{r}_1)\Psi_b(\mathbf{r}_2)\, d^3\mathbf{r} \\ &+ \int_{\substack{all\\space}} \Psi_a^*(\mathbf{r}_1)\Psi_b^*(\mathbf{r}_2) V_{ee} \Psi_a(\mathbf{r}_1)\Psi_b(\mathbf{r}_2)\, d^3\mathbf{r} \\ &= E_a^{(0)} + E_b^{(0)} + E^{(1)} \end{aligned}$$

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

$$J_{1s,1s} = \int_{\substack{all\\space}} \Psi_{1s}^*(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_1)\left(\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right)\Psi_{1s}^*(\mathbf{r}_2)\Psi(\mathbf{r}_2)\, d^3\mathbf{r} = \frac{5}{4}E_h$$

- Total energy is a sum of the unperturbed energy with the first-order correction

$$E = -\ 4\,E_h + \frac{5}{4}E_h = -\frac{11}{4}E_h = -74.8\,eV$$

Ionization potential with the Coulomb repulsion included

- The ionization potential is the measurement of the energy difference
- With the inclusion of the electron repulsion, the ionization potential is much closer to the measured value

$$He \rightarrow He^+ + e^-$$

$$\begin{aligned} \Delta E &= E_{He,1s} - E_{He,(1s)^2} \\ &= -54.4\,eV - (-74.8\,eV) \\ &= 20.4\,eV \end{aligned}$$

$$\Delta E_{\exp} = 24.6\,eV$$

Variational principle

- One can guess any approximate wave function
  - Use to calculate an approximate energy
  - Approximate energy will 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

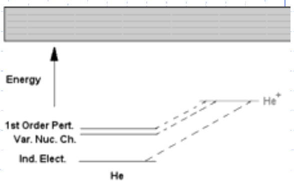
$$E_{app} = \int_{\substack{all \\ space}} \Psi^*_{app} H \Psi_{app} \, d^3\mathbf{r}$$

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

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

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, J
- 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