

Physical Chemistry

Lecture 18

Excited States of Helium; Terms

Energetics and configuration

- Helium ground state has **two** 1s electrons

$$E_{ie} = 2 E_{1s}$$

- Higher-energy configurations

$$E_{ie} = E_{1s} + E_{2s}$$

$$E_{ie} = E_{1s} + E_{2p}$$

Energy-level estimation

- Use independent-electron model as a start
- Energies of the helium-atom states estimated
- Promote electrons singly to create configurations

Independent-electron Model

1s3s	·
1s3p	·
1s3d	·
1s2s	·
1s2p	·
(1s) ²	<u>-108.8 eV</u>

Indistinguishability

- In practice, one cannot distinguish electrons by labels
 - Theory must reflect the ambiguity this fact requires
 - Interchange of labels cannot have a noticeable effect on properties like energy or electron density
- Requirement on total multi-electron wave function
 - Electrons are **fermions**, particles whose wave functions change sign upon interchange of two particles
 - Multi-electron wave functions reflect this property
 - Example of the helium atom
 - We use the interchange operator, I_{ab} , to indicate this property

$$I_{12} \Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

Application to helium-atom ground state

- Helium-atom state consists of two parts
 - Spatial part
 - Spin part

$$\Psi_{gs} = \Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)\Psi_{spin}$$

- Intechanging the electrons must change the sign of the wave function

$$I_{12} \Psi_{gs} = [I_{12} \Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)] [I_{12} \Psi_{spin}]$$

$$= [\Psi_{1s}(\mathbf{r}_2)\Psi_{1s}(\mathbf{r}_1)] [I_{12} \Psi_{spin}]$$

$$= [\Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)] [I_{12} \Psi_{spin}]$$

- Spatial part does not change sign
- Spin part must change sign

$$I_{12} \Psi_{spin} = -\Psi_{spin}$$

Indistinguishability of multi-electron spin wave functions

- The helium ground-state spatial wave function is symmetric upon interchange

$$\Psi_{gs}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)$$

- The spin part must be antisymmetric under interchange of particles

$\alpha(1)\alpha(2)$	symmetric and indistinguishable
$\alpha(1)\beta(2)$	neither symmetric nor indistinguishable
$\beta(1)\alpha(2)$	neither symmetric nor indistinguishable
$\beta(1)\beta(2)$	symmetric and indistinguishable

- Consider products of possible wave functions
- Make combinations that retain indistinguishability
- Mate antisymmetric spin combinations with symmetric spatial functions, and vice versa

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$	symmetric and indistinguishable
$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$	antisymmetric and indistinguishable

Acceptable ground-state wavefunction of helium

- ◆ Pair the symmetric space part with the antisymmetric spin part

$$\Psi_{gs}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

$$E_{gs} = 2E_{1s} + J_{1s,1s}$$

$$J_{1s,1s} = \frac{5}{4}E_h$$

First excited-state configuration of helium

- ◆ The first excited-state configuration is $(1s)^1(2s)^1$
 $\Psi_s = \frac{1}{\sqrt{2}}\{\Psi_{1s}(\mathbf{r}_1)\Psi_{2s}(\mathbf{r}_2) - \Psi_{2s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)\}$
- ◆ Have to make indistinguishable wave functions as sums and differences of products
 $\Psi_{s,spin} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$
- ◆ Have to pair up the antisymmetric and symmetric combinations to make a totally antisymmetric wave function
 $\Psi_{s,spin} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$

Spin angular momentum of multi-spin states

- ◆ Operators of the total spin angular momentum of the combined system in terms of the angular momenta of the two electrons

$$S^2 = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2)$$

$$S_z = S_{1z} + S_{2z}$$

- ◆ The linear combinations are eigenstates of the total spin angular momentum operators

$$S^2\Psi_{s,spin} = 0(0+1)\hbar^2\Psi_{s,spin} \quad S_z\Psi_{s,spin} = 0\hbar\Psi_{s,spin}$$

$$S^2\alpha(1)\alpha(2) = 1(1+1)\hbar^2\alpha(1)\alpha(2) \quad S_z\alpha(1)\alpha(2) = \hbar\alpha(1)\alpha(2)$$

$$S^2\frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\} = 1(1+1)\hbar^2\frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\} \quad S_z\frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\} = 0\hbar\frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\}$$

$$S^2\beta(1)\beta(2) = 1(1+1)\hbar^2\beta(1)\beta(2) \quad S_z\beta(1)\beta(2) = -\hbar\beta(1)\beta(2)$$

Labeling combination spin states

- ◆ The combined spin states are eigenfunctions of the total spin squared and the z component of the total spin
- ◆ Use a superscript as a label of the total spin state

S	0	1/2	1	3/2	2
Label	1	2	3	4	5
Name	singlet	doublet	triplet	quartet	quintet

Total spatial angular momentum

- ◆ Like the spin states, the combination spatial states are eigenfunctions of the total angular momentum operators, L^2 and L_z
- ◆ These eigenstates may be labeled by the value of L
 - Labels of atomic multi-electron states are capital Roman letters

L	0	1	2	3	4
Label	S	P	D	F	G

Helium-atom terms

- ◆ The eigenstate notation for the two-electron helium atom is given by the total spatial angular momentum and spin angular momentum
 $\Psi_{s^1S}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{1s}(\mathbf{r}_1)\Psi_{2s}(\mathbf{r}_2) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$
- ◆ Examples are given for the ground and first excited configurations
 $^1S = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\Psi_{2s}(2) + \Psi_{2s}(1)\Psi_{1s}(2)\} \frac{1}{\sqrt{2}}\{\alpha\beta - \beta\alpha\}$
 $^3S = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\Psi_{2s}(2) - \Psi_{2s}(1)\Psi_{1s}(2)\} \begin{bmatrix} \alpha\alpha \\ \frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\} \\ \beta\beta \end{bmatrix}$
 - "singlet S"
 - "triplet S"

Energies of first-excited-state terms

- ◆ First-order energies determined with approximate wave functions and the Hamiltonian operator

$$E_{1s} = E_{1s} + E_{2s} + J_{1s,2s} + K_{1s,2s}$$

$$E_{1s} = E_{1s} + E_{2s} + J_{1s,2s} - K_{1s,2s}$$

- ◆ Singlet and triplet energies differ because of two energy contributions from electron-electron repulsion

$$J_{1s,2s} = \frac{17}{81} Z E_h$$

$$K_{1s,2s} = \frac{16}{729} Z E_h$$

- Classical Coulomb-repulsion integral, J
- Quantum exchange integral, K

Energies of second-excited-state terms

- ◆ Second configuration arises from promotion to a 2p orbital

$$E_{1p} = E_{1s} + E_{2p} + J_{1s,2p} + K_{1s,2p}$$

$$E_{1s} = E_{1s} + E_{2p} + J_{1s,2p} - K_{1s,2p}$$

- ◆ Singlet and triplet energies differ because of electron-electron repulsion

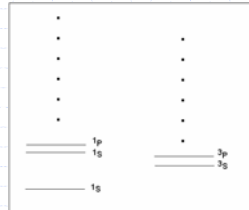
- ◆ Relative energies of these terms compared to $1S$ and $3S$ depend on the sizes of $J_{1s,2s}$ and $J_{1s,2p}$

$$J_{1s,2p} = \frac{59}{243} Z E_h$$

$$K_{1s,2p} = \frac{112}{6561} Z E_h$$

Energies of helium levels

- ◆ Energies calculated through first-order perturbation correction
- ◆ May be wrong when two levels are close in energy
- ◆ Gives relative orders
 - Lowest from $(1s)^2$
 - From $1s^1 2s^1$
 - From $1s^1 2p^1$
- ◆ Can build up higher levels by progressive increase of energy



Summary

- ◆ One may calculate energies of the helium through first order with approximate wave functions
- ◆ One may label the terms that arise from various configurations by angular momentum quantum numbers
 - Total orbital angular momentum
 - Total spin angular momentum
- ◆ Relative energies of terms depend on the sizes of the Coulomb and exchange integrals, J and K