Physical Chemistry

Lecture 18
Excited States of Helium; Terms

Energetics and configuration

- Helium ground state has **two** 1s electrons
  - Product representation gives the **configuration**
  - Configuration indicates number of electrons in each type of orbital
- Higher-energy configurations
  - Typical minimum increase in energy (to next-lowest configuration) found by promotion of a single electron to the next-lowest available single-electron energy state
  - Can find all configurations by successive promotion

$$(1s)^2$$
$$E_{ie} = 2\,E_{1s}$$

$$(1s)^1(2s)^1$$
$$E_{ie} = E_{1s} + E_{2s}$$

$$(1s)^1(2p)^1$$
$$E_{ie} = E_{1s} + E_{2p}$$

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

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1s3s
1s3p
1s3d   -66.5 eV

1s2s
1s2p   -81.6 eV

$(1s)^2$ -108.8 eV

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

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

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

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

Possible products

$\alpha(1)\alpha(2)$	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

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

1

Acceptable ground-state wavefunction of helium

◆ Pair the symmetric space part with the antisymmetric spin part

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

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

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

First excited-state configuration of helium

◆ The first excited-state configuration is $(1s)^1(2s)^1$

$$\Psi_a = \frac{1}{\sqrt{2}}\{\Psi_{1s}(r_1)\Psi_{2s}(r_2) - \Psi_{2s}(r_1)\Psi_{1s}(r_2)\}$$

$$\Psi_s = \frac{1}{\sqrt{2}}\{\Psi_{1s}(r_1)\Psi_{2s}(r_2) + \Psi_{2s}(r_1)\Psi_{1s}(r_2)\}$$

◆ Have to make indistinguishable wave functions as sums and differences of products

$$\Psi_{a,spin} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

◆ Have to pair up the antisymmetric and symmetric combinations to make a totally antisymmetric wave function

$$\alpha(1)\alpha(2)$$
$$\Psi_{s,spin} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$
$$\beta(1)\beta(2)$$

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

$$S^2 = (\mathbf{S}_1 + \mathbf{S}_2)\bullet(\mathbf{S}_1 + \mathbf{S}_2)$$
$$S_z = S_{1z} + S_{2z}$$

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

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

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

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

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

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	½	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

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

◆ Examples are given for the ground and first excited configurations

$$^1S = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\Psi_{2s}(2) + \Psi_{2s}(1)\Psi_{1s}(2)\}\frac{1}{\sqrt{2}}\{\alpha\beta - \beta\alpha\}$$

  - "singlet S"
  - "triplet S"

$$^3S = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\Psi_{2s}(2) - \Psi_{2s}(1)\Psi_{1s}(2)\}\begin{bmatrix}\alpha\alpha\\ \frac{1}{\sqrt{2}}\{\alpha\beta + \beta\alpha\}\\ \beta\beta\end{bmatrix}$$

Energies of first-excited-state terms

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

$$E_{^1S} = E_{1s} + E_{2s} + J_{1s,2s} + K_{1s,2s}$$
$$E_{^3S} = E_{1s} + E_{2s} + J_{1s,2s} - K_{1s,2s}$$

- Singlet and triplet energies differ because of two energy contributions from electron-electron repulsion
  - Classical Coulomb-repulsion integral, J
  - Quantum exchange integral, K

$$J_{1s,2s} = \frac{17}{81} Z E_h$$
$$K_{1s,2s} = \frac{16}{729} Z E_h$$

Energies of second-excited-state terms

- Second configuration arises from promotion to a 2p orbital

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

- Singler 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
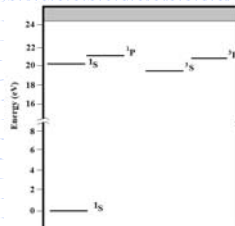
Summary

- 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