**Physical Chemistry**

**Lecture 19**

**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 available single-electron energy state
  - Can find all configurations by successive promotion

\[
(1s)^2 \\
E_{1s} = 2E_{1s}
\]

\[
(1s)^1(2s)^1 \\
E_{2s} = E_{1s} + E_{2s}
\]

**Application to helium-atom ground state**
- **Helium-atom state consists of two parts**
  - Spatial part
  - Spin part
- Introducing the electrons must change the sign of the wave function
  - Spatial part does not change sign
  - Spin part must change sign

\[
I_{12} \Psi(r_1, r_2) = - \Psi(r_2, r_1)
\]

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

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s(^1)</td>
<td>-</td>
</tr>
<tr>
<td>2s(^2)</td>
<td>46.5</td>
</tr>
<tr>
<td>2s(^1)</td>
<td>81.6</td>
</tr>
<tr>
<td>2p(^2)</td>
<td>108.8</td>
</tr>
</tbody>
</table>

**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

\[
I_{12} \Psi(r_1, r_2) = \Psi(r_2, r_1) = - \Psi(r_1, r_2)
\]

**Indistinguishability of multi-electron spin wave functions**
- The helium ground-state spatial wave function is symmetric upon interchange
- 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
Acceptable ground-state wavefunction of helium

\[ \Psi_{\text{gs}}(r_1, r_2) = \Psi_{\text{gs}}(r_1)\Psi_{\text{gs}}(r_2) \]

\[ E_{\text{gs}} = 2 E_{\text{gs}} + J_{\text{gs}} \]

\[ J_{\text{gs}} = \frac{5}{4} E_{\text{gs}} \]

First excited-state configuration of helium

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

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

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

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

<table>
<thead>
<tr>
<th>( S )</th>
<th>( 0 )</th>
<th>( \frac{1}{2} )</th>
<th>( 1 )</th>
<th>( 3/2 )</th>
<th>( 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label</td>
<td>singlet</td>
<td>doublet</td>
<td>triplet</td>
<td>quartet</td>
<td>quintet</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>( L )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label</td>
<td>S</td>
<td>P</td>
<td>D</td>
<td>F</td>
<td>G</td>
</tr>
</tbody>
</table>

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

\[ S^2 = (S_x + S_y)(S_x + S_y) \]

\[ S_x = S_x + S_y \]

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

\[ S_x \Psi_{\text{gs}} = 0 \] \( \Psi_{\text{gs}} \)

\[ S_y \Psi_{\text{gs}} = 0 \] \( \Psi_{\text{gs}} \)

\[ S_z \Psi_{\text{gs}} = 0 \] \( \Psi_{\text{gs}} \)

\[ S^2 \Psi_{\text{gs}} = 0 \] \( \Psi_{\text{gs}} \)

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</table>

Helium-atom terms

The eigenstate notation for the two-electron helium atom is given by the total spatial angular momentum and spin angular momentum

Examples are given for the ground and first excited configurations
- "singlet S"
- "triplet S"
Energies of first-excited-state terms

- First-order energies determined with approximate wave functions and the Hamiltonian operator
  \[ E_{1s} = E_{ss} + E_{or} + J_{1s,2s} + K_{1s,2s} \]
  \[ E_{1s} = E_{ss} + E_{or} + J_{1s,2s} + K_{1s,2s} \]

- 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
  \[ E_{2p} = E_{ss} + E_{or} + J_{1s,2p} + K_{1s,2p} \]
  \[ E_{2p} = E_{ss} + E_{or} + J_{1s,2p} + K_{1s,2p} \]

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

- Relative energies of these terms compared to \( ^5S \) 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 \(1s^22s^2\)
    - From \(1s^22p^2\)
  - 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 \( K \)