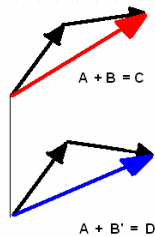# Physical Chemistry

Lecture 19

Angular Momentum of Composite Systems

Composite systems

- ◈ A quantum system such as the helium atom is a composite system
  - Parts are identifiable
  - Parts may consist of distinguishable or indistinguishable particles
- ◈ Overall properties of composite systems are derivable from the properties of components
  - Total electron density at a point is the sum of the electron densities due to the various electrons
  - Angular momentum of the total system is derivable from the angular momenta of the parts

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Adding angular momenta

- ◈ Angular momentum – a vector property
- ◈ Finding the sum of two angular momenta requires finding all possible vectors that can be produced
- ◈ Must keep in mind quantum nature of angular momentum
  - Can add only certain orientations
  - Retain uncertainty about orientation

A + B = C

A + B' = D

Angular momentum of composite system

- ◈ Must obey rules of quantum mechanical angular momentum

$$L^2\Psi = L(L+1)\hbar^2\Psi$$
$$L_z\Psi = m\hbar\,\Psi$$

- ◈ Operators for total angular momentum related to angular momentum operators of the parts of the system

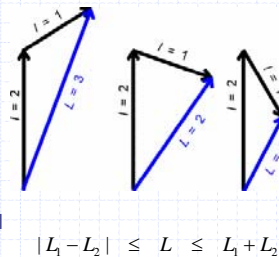$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$$
$$L^2 = \mathbf{L}\bullet\mathbf{L}$$
$$= L_1^2 + L_2^2 + 2\,\mathbf{L}_1\bullet\mathbf{L}_2$$
$$L_z = L_{1z} + L_{2z}$$

Combination of two angular momenta

- ◈ Only certain values of the total angular momentum quantum number, L
- ◈ Determined by the values of the angular momentum quantum numbers of the subparts of the system
- ◈ Can determine the total orbital angular momentum for any number of electrons combined

$$|L_1 - L_2| \le L \le L_1 + L_2$$

Orbital terms

- ◈ The orbital wave functions for multi-electron systems are simultaneous eigenfunctions of L^2 and L_z of the total system
- ◈ Multi-electron states labeled by the total angular momentum
- ◈ Use capital Roman letters

L	0	1	2	3	4	5
Symbol	S	P	D	F	G	H

Spin of multi-electron systems

- Like orbital angular momentum
- Combine spins of subparts to determine the possible values of the total spin

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

- Operators of the total system are related to the operators of the subparts

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$$
$$S^2 = \mathbf{S} \bullet \mathbf{S}$$
$$= S_1^2 + S_2^2 + 2\mathbf{S}_1 \bullet \mathbf{S}_2$$
$$S_z = S_{1z} + S_{2z}$$

- Can add more than two
  - Repeat combining operations for additional spins

Labeling spin states of composite systems

- Combined spin states are eigenfunctions of S^2 and S_z for the total system of spins
- Superscript labels the total spin state of the term

S	0	½	1	3/2	2
Label	1	2	3	4	5
Name	singlet	doublet	triplet	quartet	quintet

Pauli's exclusion principle

- In principle, one could create a configuration in which all electrons are in the lowest-energy state
  - Example: lithium atom
  - Cannot happen

$$\Psi_{spatial}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \Psi_{1s}(\mathbf{r}_1)\Psi_{1s}(\mathbf{r}_2)\Psi_{1s}(\mathbf{r}_3)$$

- Pauli's principle: there can never be two equivalent electrons in an atom for which the values of all the quantum numbers are the same.

$$\Psi_{Li,gs} = \mathscr{A}\left(\Psi_{1s}\alpha \Psi_{1s}\beta \Psi_{2s} \genfrac{}{}{0pt}{}{\alpha}{\beta} \right)$$

  - Limit on quantum numbers requires increment of principal quantum number
  - All electrons indistinguishable.
  - Requires antisymmetrization.

Degeneracies of terms

- The spatial part of the wave function has a degeneracy, g_L
- The spin part of the wave function has a degeneracy. g_S
- The total degeneracy is determined by the product of these two degeneracies

$$g = g_L \times g_S$$

State	^1S	^3S	^1P	^3P	^2S	^2D
g	1	3	3	9	2	10

Terms arising from various configurations

Configuration	S	L	Term
s^1	1/2	0	^2S
s^2	0	0	^1S
$s^1 s^1$	0 or 1	0	$^1S, {}^3S$
$s^1 p^1$	0 or 1	1	$^1P, {}^3P$
$p^1 p^1$	0 or 1	0, 1, or 2	$^1D, {}^1P, {}^1S$ $^3D, {}^3P, {}^3S$
p^2	0 or 1	0, 1, or 2	$^1S, {}^3P, {}^1D$

Unsőld's theorem

An important simplification when considering a complex system with many electrons

All closed shells can have only zero spin and zero orbital angular momentum.

Ground terms of atoms

Atom	Ground configuration	Ground term
H	$1s^1$	^2S
He	$1s^2$	^1S
Li	$1s^2 2s^1$	^2S
Be	$1s^2 2s^2$	^1S
B	$1s^2 2s^2 2p^1$	^2P
C	$1s^2 2s^2 2p^2$	^3P
N	$1s^2 2s^2 2p^3$	^4S
O	$1s^2 2s^2 2p^4$	^3P
F	$1s^2 2s^2 2p^5$	^2P
Ne	$1s^2 2s^2 2p^6$	^1S

Summary

- The labeling of states (terms) is determined by the total angular momenta of the spin and space parts of the wave function
- Atomic terms are specified by straightforward labels
- Must focus on the unfilled orbtials of the atom to determine the term symbol (application of Unsöld's theorem)