ADVANCED CHEMISTRY 2008

QUANTUM MECHANICS - SPRING - WEEK 1

Term symbols for the first 36 elements

H $1s^1$ $\underset{1s}{\underline{\uparrow}}$ $\left.\begin{array}{ll} M_L = 0 & \Rightarrow L = 0 \\ M_S = \pm\frac{1}{2} & \Rightarrow S = \frac{1}{2} \end{array}\right\}$ $J = \frac{1}{2}$

$$\underline{\underline{{}^2S_{1/2}}}$$

He $1s^2$ $\underline{\uparrow\downarrow}$ completely filled orbitals

$\Rightarrow L = 0 \quad S = 0 \quad J = 0$ $\quad \underline{\underline{{}^1S_0}}$

Li $1s^2\,2s^1$ $\underset{2s}{\underline{\uparrow}}$ $M_L = 0$ $M_S = \pm 1/2 \Rightarrow L = 0 \quad S = \frac{1}{2} \Rightarrow J = 1/2$

$$\underline{\underline{{}^2S_{1/2}}}$$

Be $1s^2\,2s^2$ completely filled orbitals $\Rightarrow L = 0,\ S = 0\ J = 0$

$$\underline{\underline{{}^1S_0}}$$

B $1s^2\,2s^2\,2p^1$ $\underset{+1}{\underline{\uparrow}}\ \underset{\underset{2p}{0}}{\underline{\quad}}\ \underset{-1}{\underline{\quad}}$ $M_L = 1$ $M_S = \pm 1/2$ $\Rightarrow L = 1 \quad S = 1/2$

$\Rightarrow J = 1/2\ ,\ 3/2$

$$\underline{\underline{{}^2P_{1/2}}} \text{ and } {}^2P_{3/2}$$

↖ ground state using Hund's rules

C $1s^2 2s^2 2p^2$ $\underset{2p}{\underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\quad}}}$ $\left.\begin{array}{l} M_L = +1 \Rightarrow L = 1 \\ M_S = \cancel{3/2}\,1 \Rightarrow S = 1 \end{array}\right\} J = 1, 0, 2$

$\underline{\underline{{}^3P_0}}$ $\quad {}^3P_1 \quad {}^3P_2$

ground state

N $1s^2 2s^2 2p^3$ $\underset{2p}{\underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}}$ $M_L = 0$ $\quad M_S = 3/2$

$L = 0$ $\quad S = 3/2 \Rightarrow J = 3/2$

$$\underline{\underline{{}^4S_{3/2}}}$$

O $1s^2 2s^2 2p^4$ $\underset{2p}{\underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}}$ $M_L = 1$ $\quad M_S = 1$

$L = 1$ $\quad S = 1$ $\quad J = 2, 1, 0$

${}^3P_0 \quad {}^3P_1 \quad \underline{\underline{{}^3P_2}}$ ground state

F $[He]\, 2s^2 2p^5$ $\underset{2p}{\underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow\downarrow}}\ \underset{-1}{\underline{\uparrow}}}$ $M_L = 1$ $\quad M_S = 1/2$

$L = 1$ $\quad S = 1/2$ $\quad J = 3/2, 1/2$

${}^2P_{1/2} \quad \underline{\underline{{}^2P_{3/2}}}$ ground state

Ne $[He]\, 2s^2 2p^6$ closed shell (completely filled orbitals)

$$\underline{\underline{{}^1S_0}}$$

Na [Ne] $3s^1$ $\underset{3s}{\underline{\ \uparrow\ }}$ $M_L = 0$ $M_S = \pm 1/2$

$L = 0$ $S = 1/2$ $\Rightarrow J = 1/2$

$$\underline{\underline{{}^2S_{1/2}}}$$

Mg [Ne] $3s^2$ closed shell $\underline{\underline{{}^1S_0}}$

Al [Ne] $3s^2 3p^1$ $\underset{3p}{\underset{+1}{\underline{\ \uparrow\ }}\ \underset{0}{\underline{\ \ \ }}\ \underset{-1}{\underline{\ \ \ }}}$ $M_L = 1$ $M_S = \pm 1/2$

$L = 1$ $S = 1/2$

$J = 3/2,\ 1/2$

${}^2P_{3/2}$ $\underline{\underline{{}^2P_{1/2}}}$ ground state

Si [Ne] $3s^2 3p^2$ $\underset{3p}{\underset{+1}{\underline{\ \uparrow\ }}\ \underset{0}{\underline{\ \uparrow\ }}\ \underset{-1}{\underline{\ \ \ }}}$ $M_L = 1$ $M_S = 1$

$L = 1$ $S = 1$ $J = 2, 1, 0$

$\underline{\underline{{}^3P_0}}$ ${}^3P_1$ ${}^3P_2$

ground state

P [Ne] $3s^2 3p^3$ $\underset{3p}{\underset{+1}{\underline{\ \uparrow\ }}\ \underset{0}{\underline{\ \uparrow\ }}\ \underset{-1}{\underline{\ \uparrow\ }}}$ $M_L = 0$ $M_S = 3/2$

$L = 0$ $S = 3/2$ $\Rightarrow J = 3/2$

$$\underline{\underline{{}^4S_{3/2}}}$$

S [Ne] $3s^2 3p^4$ $\underset{3p}{\underset{+1}{\underline{\ \uparrow\downarrow\ }}\ \underset{0}{\underline{\ \uparrow\ }}\ \underset{-1}{\underline{\ \uparrow\ }}}$ $M_L = 1$ $M_S = 1$

$L = 1$ $S = 1$ $J = 2, 1, 0$

${}^3P_0$ ${}^3P_1$ $\underline{\underline{{}^3P_2}}$ ground state.

Cl [Ne] $3s^2 3p^5$ $\underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow\downarrow}}\ \underset{-1}{\underline{\uparrow}}$ $M_L = 1$ $M_S = 1/2$

3p $L = 1$ $S = 1/2$ $J = 3/2, 1/2$

$^2P_{1/2}$ $\underline{\underline{^2P_{3/2}}}$ ground state

Ar [Ne] $3s^2 3p^6$ closed shell $\underline{\underline{^1S_0}}$

K [Ar] $4s^1$ $\underset{4s}{\underline{\uparrow}}$ $M_L = 0$ $M_S = \pm 1/2$ $L = 0$ $S = 1/2$

$J = 1/2$

$\underline{\underline{^2S_{1/2}}}$

Ca [Ar] $4s^2$ closed shell $\underline{\underline{^1S_0}}$

Sc [Ar] $4s^2 3d^1$ $\underset{+2}{\underline{\uparrow}}\ \underset{+1}{\underline{\ \ }}\ \underset{0}{\underline{\ \ }}\ \underset{-1}{\underline{\ \ }}\ \underset{-2}{\underline{\ \ }}$ $M_L = 2$ $M_S = 1/2$

3d $L = 2$ $S = 1/2$

$J = 5/2, 3/2$

$^2D_{5/2}$ $\underline{\underline{^2D_{3/2}}}$ ground state

Ti [Ar] $4s^2 3d^2$ $\underset{+2}{\underline{\uparrow}}\ \underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\ \ }}\ \underset{-1}{\underline{\ \ }}\ \underset{-2}{\underline{\ \ }}$ $M_L = 3$ $M_S = 1$

3d $L = 3$ $S = 1$

$J = 4, 3, 2$

$^3F_4$ $^3F_3$ $\underline{\underline{^3F_2}}$ ground state

V [Ar] $4s^2 3d^3$ $\underset{+2}{\underline{\uparrow}}\ \underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\ \ }}\ \underset{-2}{\underline{\ \ }}$ $M_L = 3$ $M_S = 3/2$

3d $L = 3$ $S = 3/2$

$J = 9/2, 7/2, 5/2, 3/2$

$3 + 1\frac{1}{2}$

$4\frac{1}{2}$

$^4F_{9/2}$ $^4F_{7/2}$ $^4F_{5/2}$ $\underline{\underline{^4F_{3/2}}}$ ground state

Cr [Ar]$4s^1 3d^5$ $\underset{4s}{\underline{\uparrow}}$ $\underset{+2}{\underline{\uparrow}}\ \underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}\ \underset{-2}{\underline{\uparrow}}$

3d

$M_L = 0$ $M_S = 3$

$L = 0$ $S = 3$

$J = 3$

$^7S_3$

Mn [Ar]$4s^2 3d^5$ $\underset{+2}{\underline{\uparrow}}\ \underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}\ \underset{-2}{\underline{\uparrow}}$

3d

$M_L = 0$ $M_S = 5/2$

$L = 0$ $S = 5/2$

$J = 5/2$

$^6S_{5/2}$

Fe [Ar]$4s^2 3d^6$ $\underset{+2}{\underline{\uparrow\downarrow}}\ \underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}\ \underset{-2}{\underline{\uparrow}}$

3d

$M_L = 2$ $M_S = 2$

$L = 2$ $S = 2$

$J = 4, 3, 2, 1, 0$

$^5D_4$ $^5D_3$ $^5D_2$ $^5D_1$ $^5D_0$

ground state

Co [Ar]$4s^2 3d^7$ $\underset{+2}{\underline{\uparrow\downarrow}}\ \underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}\ \underset{-2}{\underline{\uparrow}}$

3d

$M_L = 3$ $M_S = 3/2$

$L = 3$ $S = 3/2$

$J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, 3/2$

$4\frac{1}{2}$

$^4F_{9/2}$ $^4F_{7/2}$ $^4F_{5/2}$ $^4F_{3/2}$

ground state

Ni [Ar]$4s^2 3d^8$ $\underset{+2}{\underline{\uparrow\downarrow}}\ \underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow\downarrow}}\ \underset{-1}{\underline{\uparrow}}\ \underset{-2}{\underline{\uparrow}}$

3d

$M_L = 3$ $M_S = 1$

$L = 3$ $S = 1$

$J = 4, 3, 2$

$^3F_4$ $^3F_3$ $^3F_2$

ground state

Cu $[Ar]4s^1 3d^{10}$ $\underset{4s}{\underline{\uparrow}}$ $M_L = 0$ $M_S = 1/2$

$L = 0$ $S = 1/2$ $J = 1/2$

$$\underline{\underline{{}^2S_{1/2}}}$$

Zn $[Ar]4s^2 3d^{10}$ closed shell $\underline{\underline{{}^1S_0}}$

Ga $[Ar]4s^2 3d^{10} 4p^1$ $\underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\quad}}\ \underset{-1}{\underline{\quad}}$ 4p

$M_L = 1$ $M_S = 1/2$

$L = 1$ $S = 1/2$

$J = 3/2, 1/2$

$\underline{\underline{{}^2P_{1/2}}}$ ${}^2P_{3/2}$

ground state

Ge $[Ar]4s^2 3d^{10} 4p^2$ $\underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\quad}}$ 4p

$M_L = 1$ $M_S = 1$

$L = 1$ $S = 1$

$J = 2, 1, 0$

${}^3P_2$ ${}^3P_1$ $\underline{\underline{{}^3P_0}}$ ground state

As $[Ar]4s^2 3d^{10} 4p^3$ $\underset{+1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}$ 4p

$M_L = 0$ $M_S = 3/2$

$L = 0$ $S = 3/2$

$J = 3/2$

$$\underline{\underline{{}^4S_{3/2}}}$$

Se $[Ar]4s^2 3d^{10} 4p^4$ $\underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}$ 4p

$M_L = 1$ $M_S = 1$

$L = 1$ $S = 1$

$J = 2, 1, 0$

Br $[Ar]4s^2 3d^{10} 4p^5$ $\underset{+1}{\underline{\uparrow\downarrow}}\ \underset{0}{\underline{\uparrow\downarrow}}\ \underset{-1}{\underline{\uparrow}}$ $4p$ $M_L = 1$ $M_S = 1/2$

$L = 1$ $S = 1/2$

$J = 3/2, \ 1/2$

${}^2P_{1/2}$ $\underline{\underline{{}^2P_{3/2}}}$ ground state

Kr $[Ar]4s^2 3d^{10} 4p^6$ closed shell $\underline{\underline{{}^1S_0}}$

Chapter 10

(29) (a) $$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

$$\psi = \psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)$$

If we enterchange the two columns, the new wavefunction

$$\psi' = \begin{vmatrix} \psi_A(2) & \psi_A(1) \\ \psi_B(2) & \psi_B(1) \end{vmatrix} = \psi_A(2)\psi_B(1) - \psi_B(2)\psi_A(1)$$

$$= -\psi$$

$\therefore$ Interchanging the columns changes the sign of the wavefunction

Interchanging the two rows we get

$$\psi'' = \begin{vmatrix} \psi_B(1) & \psi_B(2) \\ \psi_A(1) & \psi_A(2) \end{vmatrix} = \psi_B(1)\,\psi_A(2) - \psi_A(1)\,\psi_B(2)$$

$$= -\psi$$

∴ interchanging the rows changes the sign of the wavefunction.

(c) If the two electrons have the same spin orbital, then $\psi_A(1) = \psi_B(1)$

then $$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_A(\text{[illegible]}) & \psi_A(2) \end{vmatrix} = \psi_A(1)\,\psi_A(2) - \psi_A(1)\,\psi_A(2)$$

$$= 0$$

⇒ the wavefunction is zero

⇒ the two electrons cannot have the same spin orbital.

(30) $H = 1s^1$ $\quad \underline{\underline{H^- = 1s^2}}$

$Li = 1s^2 2s^1$ $\quad \underline{\underline{Li^+ = 1s^2}}$

$O = 1s^2 2s^2 2p^4$ $\quad O^{2-} = \underline{\underline{1s^2 2s^2 2p^6}}$

$F = 1s^2 2s^2 2p^5$ $\quad F^- = \underline{\underline{1s^2 2s^2 2p^6}}$

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1s	$2\bar{e}$
2s	$2\bar{e}$
2p	$6\bar{e}$
3s	$2\bar{e}$
3p	$6\bar{e}$
3d	$10\bar{e}$

(60)

$$\psi = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)\,1s\beta(2) - 1s\alpha(2)\,1s\beta(1)$$

$$\hat{P}_{12}\psi = \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = 1s\alpha(2)\,1s\beta(1) - 1s\alpha(1)\,1s\beta(2)$$

$$= -\psi$$

since $\hat{P}_{12}\psi = -\psi$, the wavefunction is antisymmetric w.r.t. interchange of electrons.

(63) $Sc = [Ar]\,4s^2\,3d^1$

$Sc^+ = [Ar]\,4s^1\,3d^1$ $Sc^{2+} = [Ar]\,3d^1$

$Sc^{3+} = [Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$