C474B

Problem Set #7 · Solutions

(1.) a) Configuration : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p\ 4d$.

$\#$ electrons $= 2+2+6+2+6+10+2+1+1 = 32$

$\therefore$ element is germanium, Ge.

This is an excited state $\because$ ground state would have $4p^2$ configuration (all other subshells filled).

b) Closed subshells $\Rightarrow L=0,\ S=0$ $\therefore$ consider $4p4d$ configuation only

$\Rightarrow$ 2 non-equivalent electrons.

$l_1 = 1\ ;\ l_2 = 2$ $\quad\therefore L = |l_1+l_2| - |l_1-l_2|$

$= |1+2| - |1-2| = 3, 2, 1$

$s_1 = \frac{1}{2}\ ;\ s_2 = \frac{1}{2}$ $\quad\therefore S = |s_1+s_2| - |s_1-s_2|$

$= |\frac{1}{2}+\frac{1}{2}| - |\frac{1}{2}-\frac{1}{2}| = 1, 0$

$\Rightarrow 2S+1 = 3, 1$

Terms are $^{2S+1}L_J$

$\therefore$ $J = |L+S| - |L-S|$ $\Rightarrow$ $|3+1| - |3-1| = 4, 3, 2$ for $L=3, S=1$

$\Rightarrow$ $|3+0| - |3-0| = 3$ for $L=3, S=0$

$\Rightarrow$ $|2+1| - |2-1| = 3, 2, 1$ for $L=2, S=1$

$\Rightarrow$ $|2+0| - |2-0| = 2$ for $L=2, S=0$

$\Rightarrow$ $|1+1| - |1-1| = 2, 1, 0$ for $L=1, S=1$

$\Rightarrow$ $|1+0| - |1-0| = 1$ for $L=1, S=0$

$\therefore$ Terms are $^3F_4,\ ^3F_3,\ ^3F_2\ ;\ ^1F_3$

$^3D_3,\ ^3D_2,\ ^3D_1\ ;\ ^1D_2$

$^3P_2,\ ^3P_1,\ ^3P_0\ ;\ ^1P_1$

(2) a) $(nd)^2$ configuration $\Rightarrow$ 2 equivalent electron (PEP = Pauli Exclusion Principle)

#	$m_l = -2$	-1	0	1	2	M_L	M_S
1	↑↑					x	PEP
2	↓↓					x	PEP
3		↑↑				x	PEP
4		↓↓				x	PEP
5			↑↑			x	PEP
6			↓↓			x	PEP
7				↑↑		x	PEP
8				↓↓		x	PEP
9					↑↑	x	PEP
10					↓↓	x	PEP
11	↑↓					-4	0
12	↓↑					repeat	
13		↑↓				-2	0
14		↓↑				repeat	
15			↑↓			0	0
16			↓↑			repeat	
17				↑↓		2	0
18				↓↑		repeat	
19					↑↓	4	0
20					↓↑	repeat	
21	↑	↓				-3	0
22	↓	↑				-3	0
23	↑		↓			-2	0
24	↓		↑			-2	0
25	↑			↓		-1	0
26	↓			↑		-1	0
27	↑				↓	0	0
28	↓				↑	0	0
29		↑	↓			-1	0
30		↓	↑			-1	0
31		↑		↓		0	0
32		↓		↑		0	0

#	$m_l = -2$	-1	0	1	2	M_L	M_S
33		↑			↓	1	0
34		↓			↑	1	0
35			↑	↓		1	0
36			↓	↑		1	0
37			↑		↓	2	0
38			↓		↑	2	0
39				↑	↓	3	0
40				↓	↑	3	0
41	↑	↑				-3	1
42	↓	↓				-3	1
43	↑		↑			-2	1
44	↓		↓			-2	-1
45	↑			↑		-1	1
46	↓			↓		-1	-1
47	↑				↑	0	1
48	↓				↓	0	-1
49		↑	↑			-1	1
50		↓	↓			-1	-1
51		↑		↑		0	1
52		↓		↓		0	-1
53		↑			↑	1	1
54		↓			↓	1	-1
55			↑	↑		1	1
56			↓	↓		1	-1
57			↑		↑	2	1
58			↓		↓	2	-1
59				↑	↑	3	1
60				↓	↓	3	-1

Slater Diagram   MAX $M_L = 4$ MIN $M_L = -4$
MAS $M_L = 1$ MIN $M_L = -1$

$M_S \backslash M_L$	−4	−3	−2	−1	0	1	2	3	4
−1	–	I	I	II	II	II	I	I	I
0	I	II	III	III	IIIII	IIII	III	II	I
1	–	I	I	II	II	II	I	I	–

Terms: ^3F, ^3P, ^1G, ^1D, ^1S

$J = |3+1| - |3-1| = 4, 3, 2$ for $L = 3$, $S = 1$
$J = |1+1| - |1-1| = 2, 1, 0$ for $L = 1$, $S = 1$
$J = |4+0| - |4-0| = 4$ for $L = 4$, $S = 0$
$J = |2+0| - |2-0| = 2$ for $L = 2$, $S = 0$
$J = |0+0| - |0-0| = 0$ for $L = 0$, $S = 0$

parity $= (-1)^{\sum l_i}$
$= (-1)^{2+2} = +1$
$\Rightarrow$ even

$\Rightarrow {}^{2S+1}L_J = {}^3F_4, {}^3F_3, {}^3F_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1G_4, {}^1D_2, {}^1S_0$

b) $(nd)^2 np$ Have the $(nd)^2$ terms from part a).
np is a non-equivalent electron. $l_3 = 1$, $s_3 = 1/2$

$\therefore$ i) $^3F + np \Rightarrow L = |3+1| - |3-1| = 4, 3, 2$
$S = |1+1/2| - |1-1/2| = 3/2, 1/2$
$2S+1 = 4, 2$

${}^{2S+1}L = {}^4G, {}^2G, {}^4F, {}^2F, {}^4D, {}^2D$

$J = |4+3/2| - |4-3/2| = 11/2, 9/2, 7/2, 5/2$ for $L = 4$, $S = 3/2$
$J = |4+1/2| - |4-1/2| = 9/2, 7/2$ for $L = 4$, $S = 1/2$
$J = |3+3/2| - |3-3/2| = 9/2, 7/2, 5/2, 3/2$ for $L = 3$, $S = 3/2$
$J = |3+1/2| - |3-1/2| = 7/2, 5/2$ for $L = 3$, $S = 1/2$
$J = |2+3/2| - |2-3/2| = 7/2, 5/2, 3/2, 1/2$ for $L = 2$, $S = 3/2$
$J = |2+1/2| - |2-1/2| = 3/2, 1/2$ for $L = 2$, $S = 1/2$

${}^{2S+1}L_J = {}^4G_{11/2}, {}^4G_{9/2}, {}^4G_{7/2}, {}^4G_{5/2}, {}^2G_{9/2}, {}^2G_{7/2}, {}^4F_{9/2}, {}^4F_{7/2}, {}^4F_{5/2}, {}^4F_{3/2}$
${}^2F_{7/2}, {}^2F_{5/2}, {}^4D_{7/2}, {}^4D_{5/2}, {}^4D_{3/2}, {}^4D_{1/2}, {}^2D_{3/2}, {}^2D_{1/2}$.

ii) $^3P + np \Rightarrow L = |1+1| - |1-1| = 2, 1, 0$

$S = 3/2, 1/2 \Rightarrow 2s+1 = 4, 2$ again.

$\Rightarrow {}^{2s+1}L = {}^4D, {}^2D, {}^4P, {}^2P, {}^4S, {}^2S.$

$\Rightarrow {}^{2s+1}L_J = {}^4D_{7/2}, {}^4D_{5/2}, {}^4D_{3/2}, {}^4D_{1/2}, {}^2D_{3/2}, {}^2D_{1/2}$

$J = |1+3/2| - |1-3/2| = 5/2, 3/2, 1/2 = {}^4P_{5/2}, {}^4P_{3/2}, {}^4P_{1/2} \quad (L=1, S=3/2)$

$J = |1+1/2| - |1-1/2| = 3/2, 1/2 = {}^2P_{3/2}, {}^2P_{1/2} \quad (L=1, S=1/2)$

$J = |0+3/2| - |0-3/2| = 3/2 = {}^4S_{3/2} \quad (L=0, S=3/2)$

$J = |0+1/2| - |0-1/2| = 1/2 = {}^2S_{1/2} \quad (L=0, S=1/2)$

iii) $^1G + np \Rightarrow L = |4+1| - |4-1| = 5, 4, 3$

$S = |0+1/2| - |0-1/2| = 1/2 \Rightarrow 2s+1 = 2$

$\therefore {}^{2s+1}L = {}^2H, {}^2G, {}^2F$

$J = |5+1/2| - |5-1/2| = 11/2, 9/2 \Rightarrow {}^2H_{11/2}, {}^2H_{9/2} \quad (L=4, S=1/2)$

$J = |4+1/2| - |4-1/2| = 9/2, 7/2 \Rightarrow {}^2G_{9/2}, {}^2G_{7/2} \quad (L=3, S=1/2)$

$J = |3+1/2| - |3-1/2| = 7/2, 5/2 \Rightarrow {}^2F_{7/2}, {}^2F_{5/2} \quad (L=2, S=1/2).$

iv) $^1D + np \Rightarrow L = |2+1| - |2-1| = 3, 2, 1, \quad 2S+1 = 2$

$\therefore {}^{2s+1}L = {}^2F, {}^2D, {}^2P$

$J = |3+1/2| - |3-1/2| = 7/2, 5/2 \Rightarrow {}^2F_{7/2}, {}^2F_{5/2} \quad (L=3, S=1/2)$

$J = |2+1/2| - |2-1/2| = 5/2, 3/2 \Rightarrow {}^2D_{5/2}, {}^2D_{3/2} \quad (L=2, S=1/2)$

$J = |1+1/2| - |1-1/2| = 3/2, 1/2 \Rightarrow {}^2P_{3/2}, {}^2P_{1/2} \quad (L=1, S=1/2)$

v) $^1S + np \Rightarrow L = |0+1| - |0-1| = 1, \quad 2s+1 = 2$

$\therefore {}^{2s+1}L = {}^2P$

$J = |1+1/2| - |1-1/2| = 3/2, 1/2 \Rightarrow {}^2P_{3/2}, {}^2P_{1/2} \quad (L=1, S=1/2).$

Parity of terms $= (-1)^{\sum l_i} = (-1)^{2+2+1} = (-1)^5 = -1 \Rightarrow$ odd.

Summary: ${}^4G^o_{11/2, 9/2, 7/2, 5/2}$; ${}^4F^o_{9/2, 7/2, 5/2, 3/2}$;

$2\times({}^4D^o_{7/2, 5/2, 3/2, 1/2})$; ${}^4P^o_{5/2, 3/2, 1/2}$; ${}^4S^o_{3/2}$, ${}^2H^o_{11/2, 9/2}$

$2\times({}^2G^o_{9/2, 7/2})$; $3\times({}^2F^o_{7/2, 5/2})$; $3\times({}^2D^o_{5/2, 3/2})$, $3\times({}^2P^o_{3/2, 1/2})$

${}^2S^o_{1/2}$.

3. $(np)^3$ configuration   3 equivalent electrons

#	$m_\ell = -1$	0	1	M_L	M_S
1	↑ ↑	↑		x	PEP
2	↓ ↓	↑		x	PEP
3	↑ ↑	↓		x	PEP
4	↓ ↓	↓		x	PEP
5	↑ ↑		↑	x	PEP
6	↓ ↓		↑	x	PEP
7	↑ ↑		↓	x	PEP
8	↓ ↓		↓	x	PEP
9		↑ ↑	↑	x	PEP
10		↓ ↓	↑	x	PEP
11		↑ ↑	↓	x	PEP
12		↓ ↓	↓	x	PEP
13	↑	↑ ↑		x	PEP
14	↑	↓ ↓		x	PEP
15	↓	↑ ↑		x	PEP
16	↓	↓ ↓		x	PEP
17	↑		↑ ↑	x	PEP
18	↑		↓ ↓	x	PEP
19	↓		↑ ↑	x	PEP
20	↓		↓ ↓	x	PEP
21		↑	↑ ↑	x	PEP
22		↑	↓ ↓	x	PEP
23		↓	↑ ↑	x	PEP
24		↓	↓ ↓	x	PEP
25	↑ ↓	↑		−2	½
26	↓ ↑	↑		repeat	
27	↑ ↓	↓		−2	−½
28	↓ ↑	↓		repeat	
29	↑ ↓		↑	−1	½
30	↓ ↑		↑	repeat	
31	↑ ↓		↓	−1	−½
32	↓ ↑		↓	repeat	

#	$m_\ell = -1$	0	1	M_L	M_S
33	↑	↑ ↓		-1	$1/2$
34	↑	↓ ↑		repeat →	
35	↓	↑ ↓		-1	$-1/2$
36	↓	↓ ↑		repeat →	
37		↑ ↓	↑	1	$1/2$
38		↓ ↑	↑	repeat →	
39		↑ ↓	↓	1	$-1/2$
40		↓ ↑	↓	repeat →	
41	↑		↑ ↓	1	$1/2$
42	↑		↓ ↑	repeat →	
43	↓		↑ ↓	1	$-1/2$
44	↓		↓ ↑	repeat →	
45		↑	↑ ↓	2	$1/2$
46		↑	↓ ↑	repeat →	
47		↓	↑ ↓	2	$-1/2$
48		↓	↓ ↑	repeat →	
49	↑	↑	↑	0	$3/2$
50	↑	↓	↑	0	$1/2$
51	↑	↑	↓	0	$1/2$
52	↑	↓	↓	0	$-1/2$
53	↓	↑	↑	0	$1/2$
54	↓	↑	↓	0	$-1/2$
55	↓	↓	↑	0	$-1/2$
56	↓	↓	↓	0	$-3/2$

MAX $M_L = 2$ MIN $M_L = -2$

MAX $M_S = 3/2$ MIN $M_S = -3/2$

Slater diagram

$M_S \backslash M_L$	-2	-1	0	1	2
$3/2$	–	–	I	–	–
$1/2$	I	II	III	II	I
$-1/2$	I	II	III	II	I
$-3/2$	–	–	I	–	–

$S = 3/2, 1/2 \Rightarrow 2S+1 = 4, 2$ ∴ Terms are ^4S, ^2D, ^2P

$-3/2$

$J = |0 + 3/2| - |0 - 3/2| = 3/2 \Rightarrow {}^4S_{3/2}$ (for $L = 0$, $S = 3/2$)

$J = |2 + 1/2| - |2 - 1/2| = 5/2, 3/2 \Rightarrow {}^2D_{5/2}, {}^2D_{3/2}$ ($L = 2$, $S = 1/2$)

$J = |1 + 1/2| - |1 - 1/2| = 3/2, 1/2 \Rightarrow {}^2P_{3/2}, {}^2P_{1/2}$ ($L = 1$, $S = 1/2$)

parity $= (-1)^{\sum_i l_i} = (-1)^{1+1+1} = (-1)^3 = -1 \Rightarrow$ odd parity

${}^{2S+1}L_J = {}^4S^o_{3/2}, \; {}^2P^o_{3/2}, \; {}^2P_{1/2}, \; {}^2D^o_{5/2}, \; {}^2D^o_{3/2}$