LS, *JK*, and *jj* Atomic Spectroscopic Terms and Spectroscopic Terms for small molecules

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LS (Russell-Saunders) coupling

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X Brazilian Meeting on Rare Earths, BMRE-2024
III Workshop on Theoretical Bioinorganic Chemistry, WTBC-2024
September 12th - 15th, 2024

The noblest pleasure
is the joy of understanding.

Leonardo da Vinci

References

Basic books

Any book on inorganic chemistry

- Weller, M.; Overton, T.; Rourke, J.; Armstrong, F. *Inorganic Chemistry*, 6th ed., Oxford University Press, 2014.

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- Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 3rd. ed., John Wiley & Sons, Inc, 1994.

Basic books

Any book on inorganic chemistry

- Pfennig, B. W. *Principles of Inorganic Chemistry*, Wiley, 2015.

Basic books

Any book on physical chemistry

- Pilar, F. L. *Elementary Quantum Chemistry*, McGraw–Hill Book Company, 1968.

- Levine, I. N. *Quantum Chemistry*, 4th ed., Prentice-Hall, 1991.

Advanced books

- Harris, D. C.; Bertolucci, M. D. *Symmetry and Spectroscopy*, Oxford, 1978

- Cowan, R. D. *The Theory of Atomic Structure and Spectra*, University of California Press, 1981.

- Bernath, P. F. *Spectra of Atoms and Molecules*, 3rd, ed., Oxford University Press, 2016.

Articles on *LS* coupling

- Russell, H. N. On the calculation of the spectroscopic terms derived from equivalent electrons, *Phys. Rev.* **1927**, *29*(6), 782-789. DOI: 10.1103/PhysRev.29.782

- Gibbs, R. C.; Wilber, D. T.; White, H. E. Terms arising from similar and dissimilar electrons, *Phys. Rev.* **1927**, *29*, 790-793. DOI: 10.1103/PhysRev.29.790

- Hyde, K. E. Methods for Obtaining Russell–Sauders Term Symbols from Electronic configurations, *J. Chem. Educ.* **1975**, *52*, 87–89. DOI: 10.1021/ed052p87

Articles on *jj* coupling

- Gauerke, E. S. J.; Campbell, M. L. A Simple, Systematic Method for Determining J Levels for jj Coupling, *J. Chem. Educ.* **1994**, *71*, 457-463. DOI: 10.1021/ed071p457

- Haigh, C. W. The Theory of Atomic Spectroscopy: jj Coupling, Intermediate Coupling, and Configuration Interaction, *J. Chem. Educ.* **1995**, *72*, 206-210. DOI: 10.1021/ed072p206

- Campbell, M. L. Rules for Determining the Ground State of a *j-j* Coupled Atom, *J. Chem. Educ.* **1998**, *75*, 1339-1340. DOI: 10.1021/ed075p1339

Articles on *jj* coupling

- Orofino, H.; Faria, R. B. Obtaining the Electron Angular Momentum Coupling Spectroscopic Terms, jj, *J. Chem. Educ.* **2010**, *87*, 1451-1454. DOI: 10.1021/ed1004245

LS and *jj* comparison

- Dias, L. A. L.; Cardozo, T. M.; Faria, R. B. The Role of jj Coupling on the Energy Levels of Heavy Atoms, *Quim. Nova* **2025**, *48*(1):e-20250006, 1-7. DOI: 10.21577/0100-4042.20250006

Site for energy levels and line spectra of elements and ions

NIST, National Institute of Standard and Technology, Atomic Spectra Database, https://www.nist.gov/pml/atomic-spectra-database

LS coupling

Russell-Sauders coupling

LS coupling

The interaction between the vectors spin angular momentum of an electron (***s***) and its own orbital angular momentum (***ℓ***) is called **spin-orbit coupling**.

In the ***LS* coupling** case, the electrostatic interactions (Coulomb interaction) between electrons are much stronger than the spin-orbit coupling.

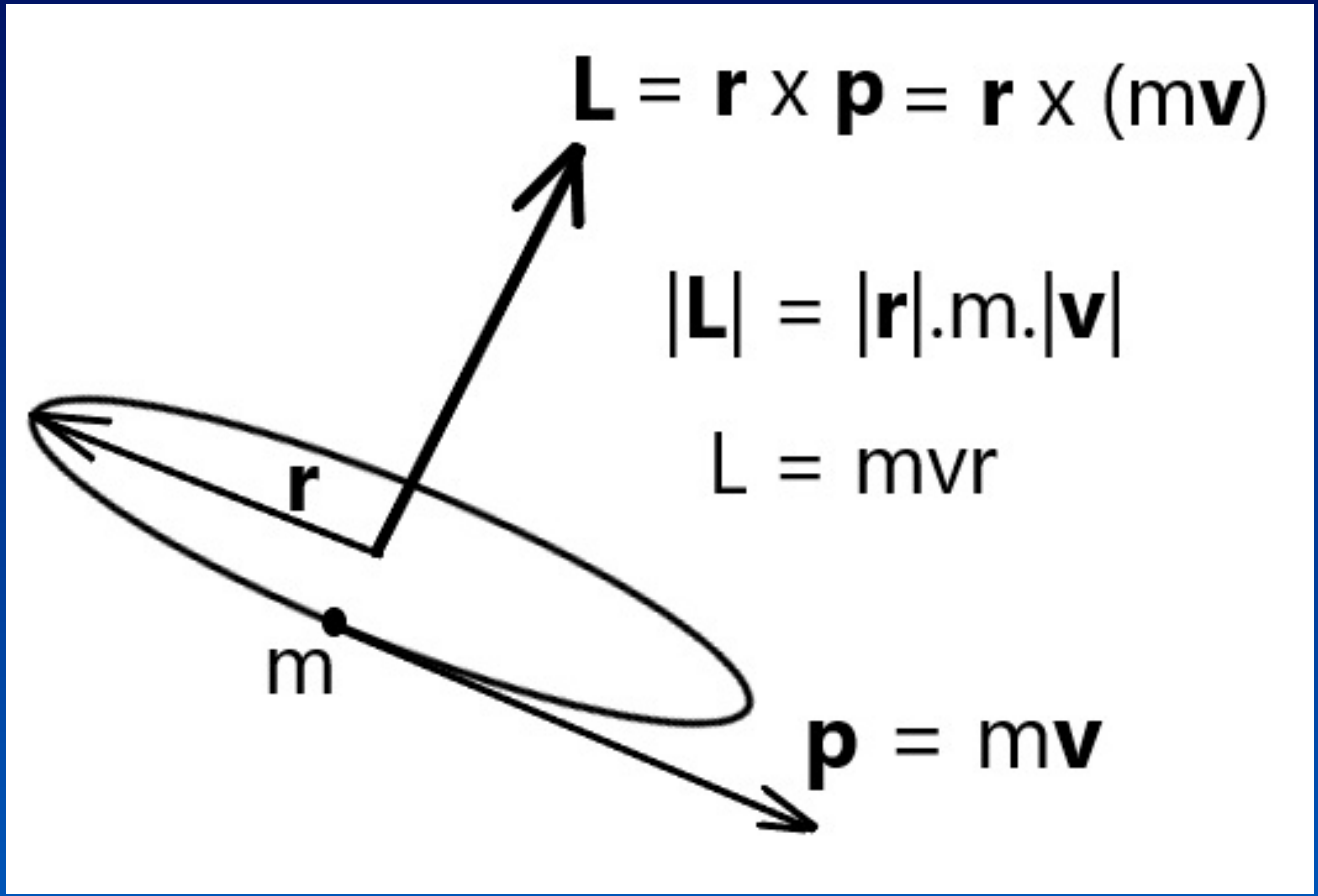
The *LS* coupling is more appropriate for light elements.

LS coupling

The ***LS* coupling** is based on the atom

- angular orbital momentum
- angular spin momentum
- total angular momentum

Angular momentum



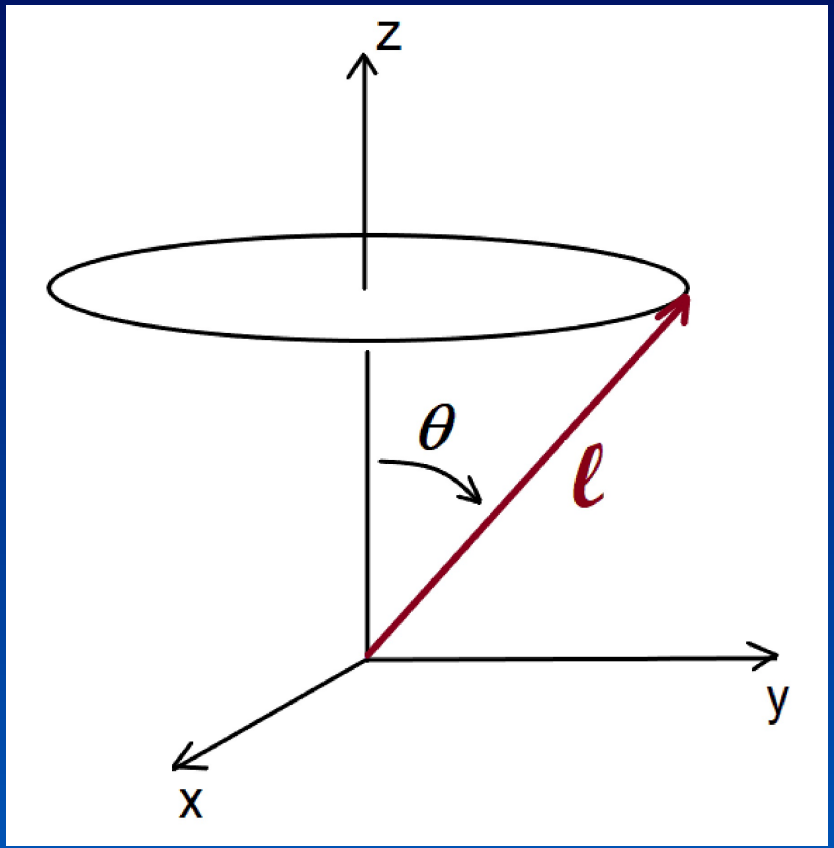
Angular momentum in quantum mechanics

$$|\vec{l}| = \sqrt{l(l+1)}\,\frac{h}{2\pi} \qquad |\vec{L}| = \sqrt{L(L+1)}\,\frac{h}{2\pi}$$

$$|\vec{s}| = \sqrt{s(s+1)}\,\frac{h}{2\pi} \qquad |\vec{S}| = \sqrt{S(S+1)}\,\frac{h}{2\pi}$$

$$|\vec{j}| = \sqrt{j(j+1)}\,\frac{h}{2\pi} \qquad |\vec{J}| = \sqrt{J(J+1)}\,\frac{h}{2\pi}$$

Angular momentum



$$\theta = \cos^{-1}\left(\frac{m_l}{\sqrt{l(l+1)}}\right)$$

LS coupling

Quantum numbers

- the orbital angular momentum of the atom, L
- the spin angular momentum of the atom, S
- total the total angular momentum of the atom, J

LS coupling

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

spin multiplicity = $2S+1$

	0	1	2	3	4	5	6	7	8	9	10	11 ...
ℓ (for electrons)	s	p	d	f	g	h	i	k	l	m	n	o ...
L (for atoms)	S	P	D	F	G	H	I	K	L	M	N	O...

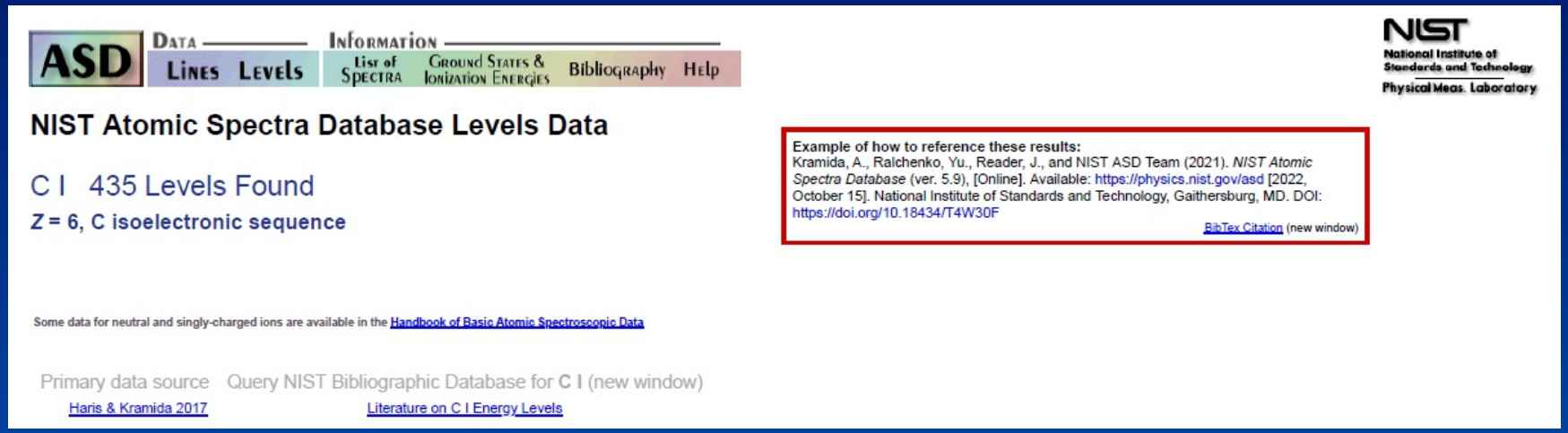
j and J are intentionally missing

LS coupling

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

Each term symbol corresponds to an energy level of the atom.

LS terms for carbon



ASD Data — Lines Levels Information — List of Spectra Ground States & Ionization Energies Bibliography Help

NIST National Institute of Standards and Technology Physical Meas. Laboratory

NIST Atomic Spectra Database Levels Data

C I 435 Levels Found

Z = 6, C isoelectronic sequence

Example of how to reference these results:
Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2021). *NIST Atomic Spectra Database* (ver. 5.9), [Online]. Available: https://physics.nist.gov/asd [2022, October 15]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W30F

BibTex Citation (new window)

Some data for neutral and singly-charged ions are available in the Handbook of Basic Atomic Spectroscopic Data

Primary data source: Haris & Kramida 2017

Query NIST Bibliographic Database for **C I** (new window): Literature on C I Energy Levels

LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*
$2s^2 2p3s$	$^3P^\circ$	0	1	*60 333.4476*
		1	3	*60 352.6584*
		2	5	*60 393.1693*
$2s^2 2p3s$	$^1P^\circ$	1	3	*61 981.83211*
$2s2p^3$	$^3D^\circ$	3	7	*64 086.96961*
		1	3	*64 089.8990*
		2	5	*64 090.99351*

LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*

LS coupling - p^2 electronic configuration

Douglas and McDaniel method

1. Built the microstates
2. Add the m_l values to obtain a M_L value
3. Compute all possible M_S values as Σm_s
4. Built the ocorrence table
5. Extract the terms

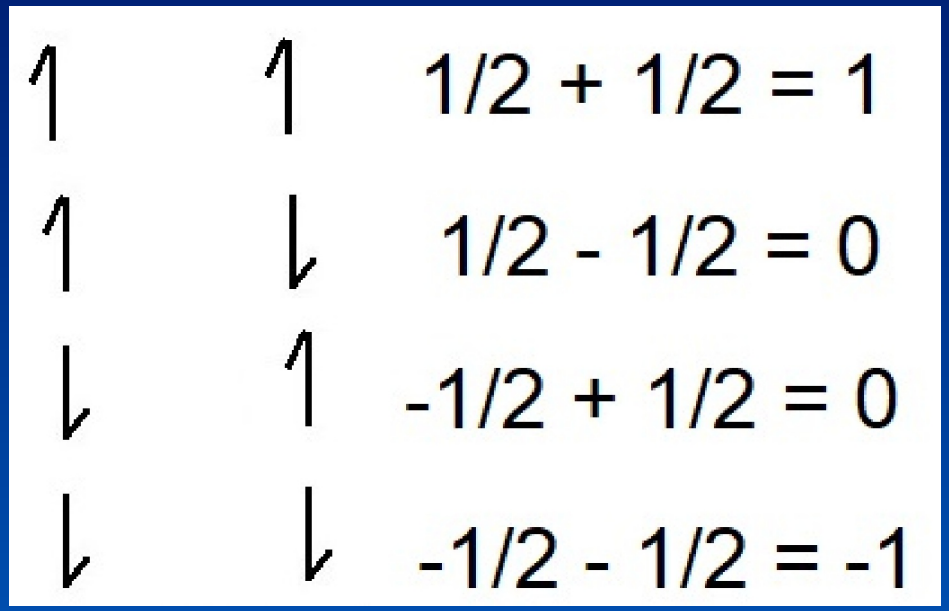
LS coupling - p^2 electronic configuration

Building the microstates

$m_l = 1$	$m_l = 0$ p_z	$m_l = -1$	$M_L = \sum m_l$	$M_S = \sum m_s$
x x			2	0
	x x		0	0
		x x	-2	0
x	x		1	1, 0, 0, -1
x		x	0	1, 0, 0, -1
	x	x	-1	1, 0, 0, -1

LS coupling - p^2 electronic configuration

Computing all possible M_S values as Σm_s



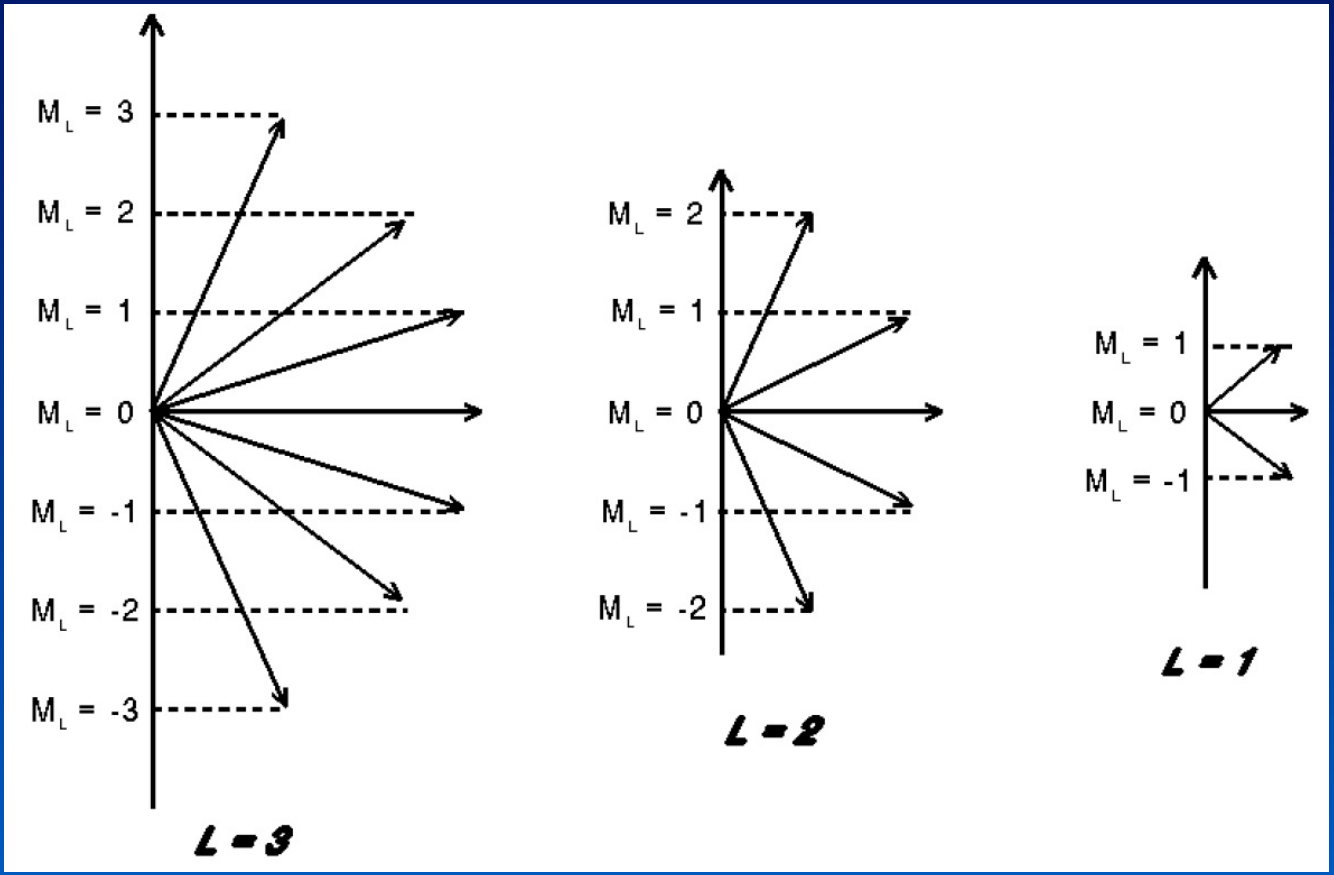
LS coupling - p^2 electronic configuration

Counting the microstates

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$		1	
$M_L = 1$	1	2	1
$M_L = 0$	1	3	1
$M_L = -1$	1	2	1
$M_L = -2$		1	

LS coupling - p^2 electronic configuration

The vector model



LS coupling - p^2 electronic configuration

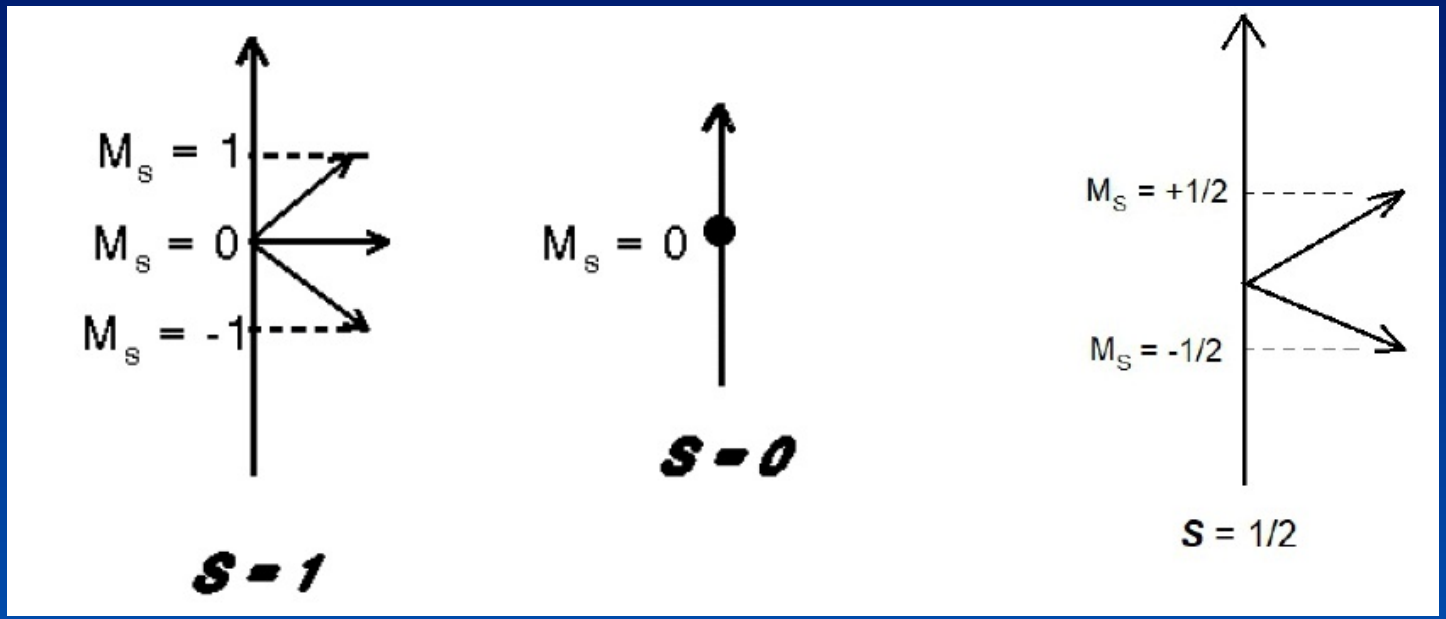
Extracting the term symbols

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$		1	
$M_L = 1$	1	2	1
$M_L = 0$	1	3	1
$M_L = -1$	1	2	1
$M_L = -2$		1	

In the column $M_S = 0$ we see that M_L spans from 2 to -2, indicating that $L = 2$, which corresponds to a term D

LS coupling - p^2 electronic configuration

The vector model



LS coupling - p^2 electronic configuration

Extracting the term symbols

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$		1	
$M_L = 1$	1	2	1
$M_L = 0$	1	3	1
$M_L = -1$	1	2	1
$M_L = -2$		1	

For $L = 2$, only the column $M_S = 0$ is used. It means that $S = 0$ and the spin multiplicity $2S + 1 = 1$, a singlet state, indicated by the term symbol ^1D

LS coupling - p^2 electronic configuration

Obtaining the *J* values

The total angular momentum *J* may have several values in the range

$$J = L+S, L+S-1, L+S-2, \ldots , |L-S|$$

As $L = 2$ and $S = 0$, the unique value for *J* is 2, given the term symbol

$$^1D_2$$

LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*

LS coupling - p^2 electronic configuration

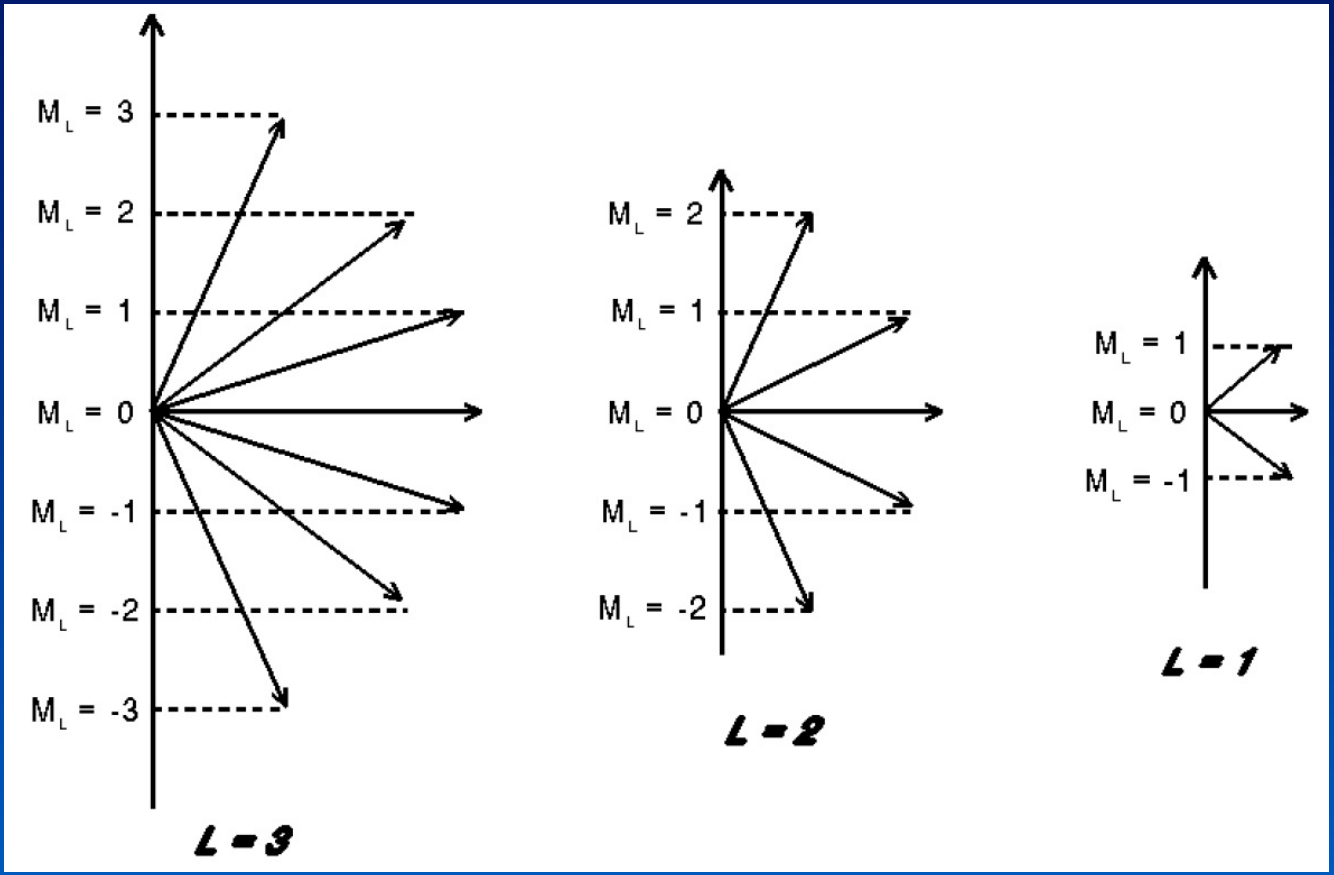
Removing the contribution of $^1D_2$ term from the central column we obtain

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$			
$M_L = 1$	1	1	1
$M_L = 0$	1	2	1
$M_L = -1$	1	1	1
$M_L = -2$			

All lines go from $M_L = 1$ until $M_L = -1$, indicating a value of $L = 1$, which corresponds to a P symbol.

LS coupling - p^2 electronic configuration

The vector model



LS coupling - p^2 electronic configuration

Extracting the term symbols

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$			
$M_L = 1$	1	1	1
$M_L = 0$	1	2	1
$M_L = -1$	1	1	1
$M_L = -2$			

All columns go from $M_S = 1$ until $M_S = -1$, indicating a value of $S = 1$, and the spin multiplicity $2S + 1 = 3$, a triplet state, indicated by the term symbol ^3P

LS coupling - p^2 electronic configuration

Obtaining the *J* values

$$J = L+S, L+S-1, L+S-2, \ldots , |L-S|$$

As $L = 1$ and $S = 1$, the J values are 2, 1, and 0, resulting in the term symbol

$$^3P_{2,1,0}$$

LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*

LS coupling - p^2 electronic configuration

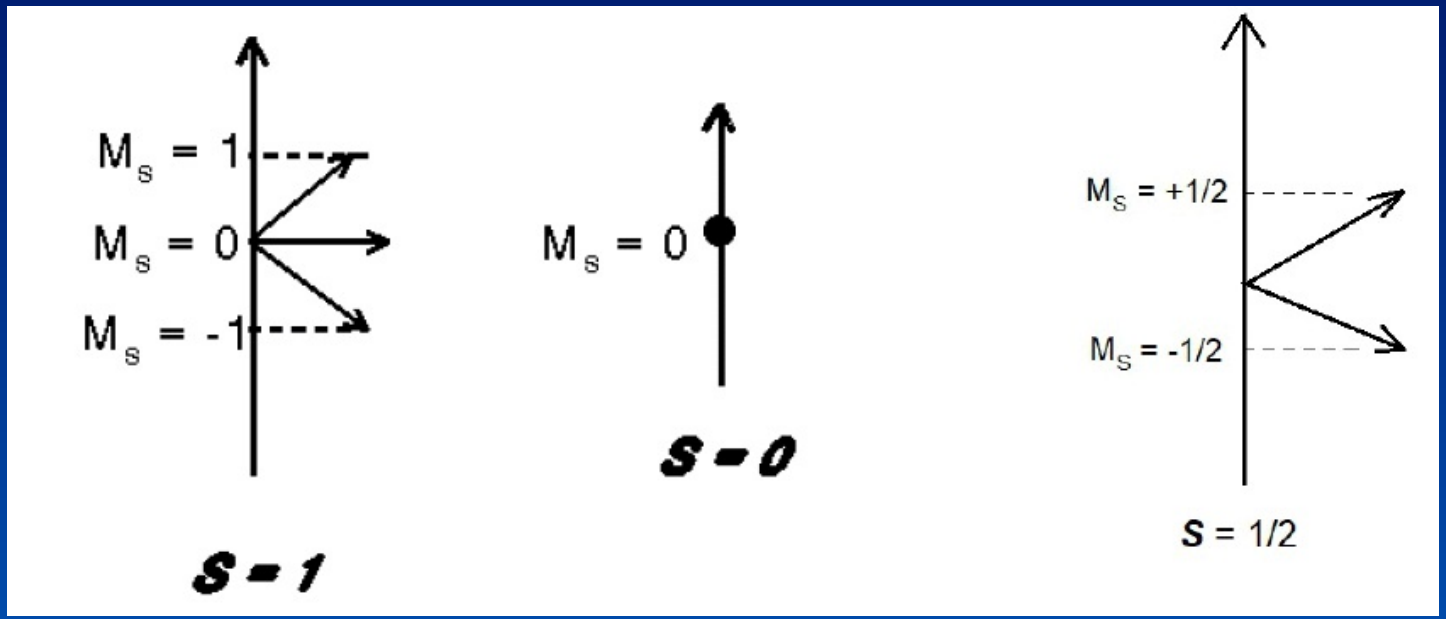
Extracting the term symbols

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$			
$M_L = 1$			
$M_L = 0$		1	
$M_L = -1$			
$M_L = -2$			

As the unique line has the value $M_L = 0$, it means that $L = 0$, which corresponds to a S symbol.

LS coupling - p^2 electronic configuration

The vector model



LS coupling - p^2 electronic configuration

Extracting the term symbols

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 2$			
$M_L = 1$			
$M_L = 0$		1	
$M_L = -1$			
$M_L = -2$			

As only the column used has the value $M_S = 0$, it means that $S = 0$ and the spin multiplicity, $2S + 1 = 1$, a singlet state, which gives the term symbol ^1S.

LS coupling - p^2 electronic configuration

Obtaining the *J* values

The total angular momentum *J* may have several values in the range

$$J = L+S, L+S-1, L+S-2, \ldots , |L-S|$$

As $L = 0$ and $S = 0$, the unique *J* value is 0, and the resulting term symbol is

$$^1S_0$$

LS coupling - p^2 electronic configuration

Colecting all terms

$^1D_2$ $^3P_{2,1,0}$ $^1S_0$

LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*

LS coupling - p^2 electronic configuration

Hund's rules

- Hund's rules are empirical rules which are valid only for the lowest energy term.

- The Hund's rules are applied once to determine the lower energy term, and cannot be applied to other terms of higher energy.

LS coupling - p^2 electronic configuration

Hund's rules

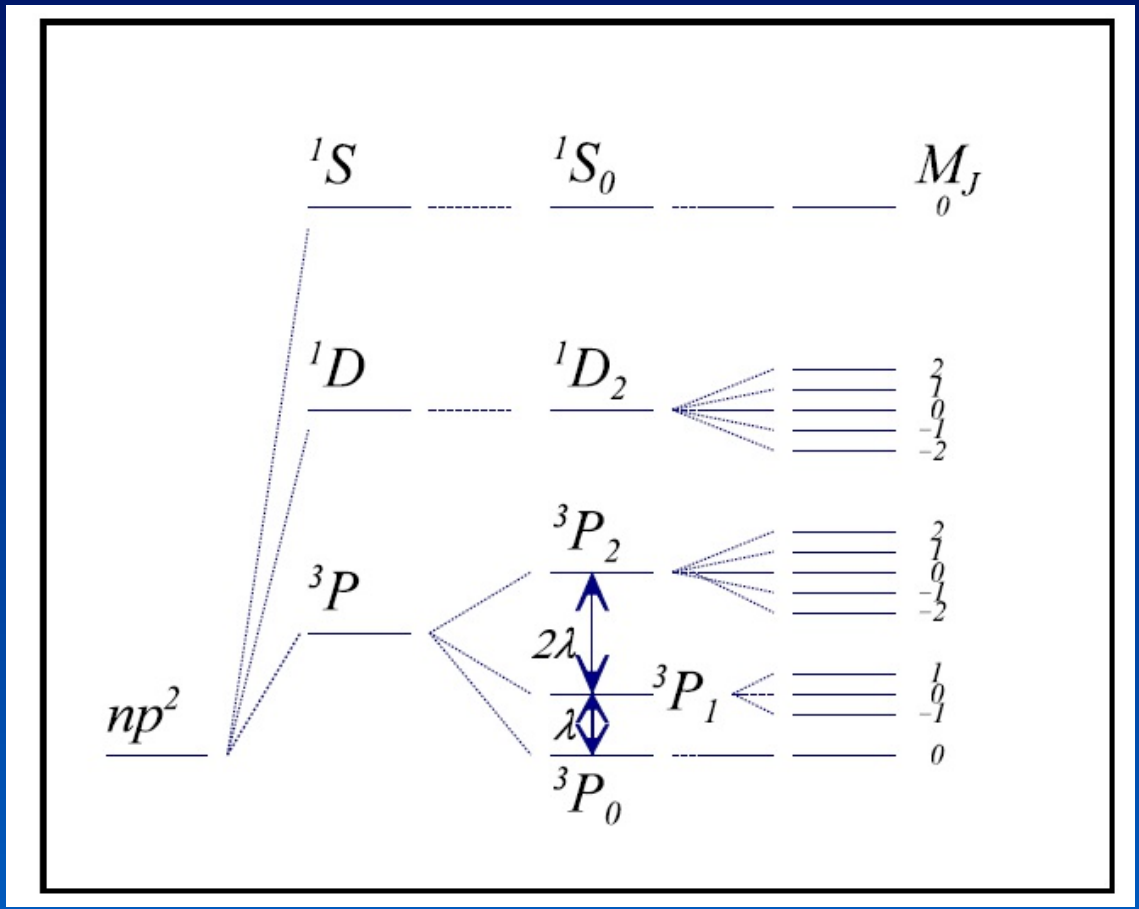
1) The term with the highest spin multiplicity is the lower energy term.

2) For electronic configurations less than half filled, the lower *J* has the lower energy.

- As a result, the lowest energy term is $^3P_0$
- The sequency of energy of the other terms can be determined by other methods, but not by the use of the Hund's rules

LS coupling - p^2 electronic configuration

Energy levels for a p^2 electronic configuration

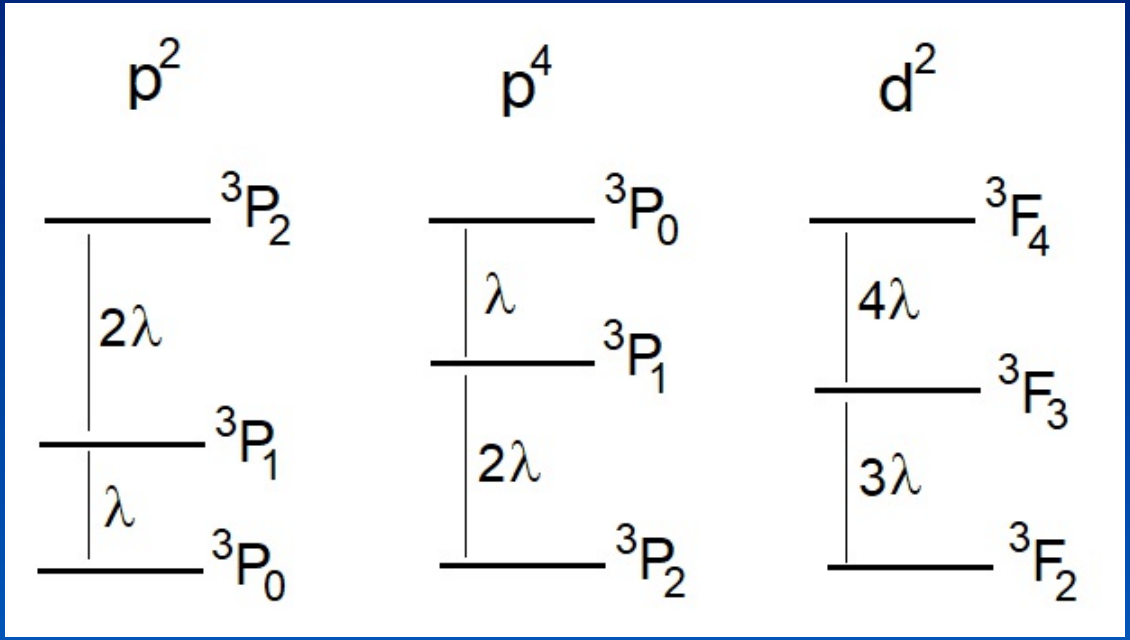


LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	*33 735.121*

The Landé interval rule

The separation between different levels in a multiplet is proportional to the highest *J* value.



LS terms for carbon

Configuration	Term	*J*	*g*	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	1	0.0000000
		1	3	16.4167130
		2	5	43.4134567
$2s^2 2p^2$	^1D	2	5	10 192.657
$2s^2 2p^2$	^1S	0	1	21 648.030
$2s2p^3$	$^5S^\circ$	2	5	33 735.121
$2s^2 2p3s$	$^3P^\circ$	0	1	60 333.4476
		1	3	60 352.6584
		2	5	60 393.1693
$2s^2 2p3s$	$^1P^\circ$	1	3	61 981.83211
$2s2p^3$	$^3D^\circ$	3	7	64 086.96961
		1	3	64 089.8990

Landé interval

16,416 = λ

16,416 × 2 = 32,832 = 2λ

43,413 -16,416 = 26,997 = 2λ

26,997 / 2 = 13,498 = λ

LS coupling - d^2 electronic configuration

$m_l = 2$	$m_l = 1$	$m_l = 0$	$m_l = -1$	$m_l = -2$	$M_L = \sum m_l$	$M_S = \sum m_s$
x x					4	0
	x x				2	0
		x x			0	0
			x x		-2	0
				x x	-4	0
x	x				3	1,0,0,-1
x		x			2	1,0,0,-1
x			x		1	1,0,0,-1
x				x	0	1,0,0,-1
	x	x			1	1,0,0,-1
	x		x		0	1,0,0,-1
	x			x	-1	1,0,0,-1
		x	x		-1	1,0,0,-1
		x		x	-2	1,0,0,-1
			x	x	-3	1,0,0,-1

Building the microstates

LS coupling - d^2 electronic configuration

Counting the microstates

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 4$		1	
$M_L = 3$	1	2	1
$M_L = 2$	1	3	1
$M_L = 1$	2	4	2
$M_L = 0$	2	5	2
$M_L = -1$	2	4	2
$M_L = -2$	1	3	1
$M_L = -3$	1	2	1
$M_L = -4$		1	

In the column $M_S = 0$ we see that M_L spans from 4 to -4, indicating that $L = 4$, which corresponds to a term G

LS coupling

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

spin multiplicity = 2S+1

	0	1	2	3	4	5	6	7	8	9	10	11 ...
ℓ (for electrons)	s	p	d	f	g	h	i	k	l	m	n	o ...
L (for atoms)	S	P	D	F	G	H	I	K	L	M	N	O...

j and J are intentionally missing

LS coupling - d^2 electronic configuration

Extracting the term symbol

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 4$		1	
$M_L = 3$	1	2	1
$M_L = 2$	1	3	1
$M_L = 1$	2	4	2
$M_L = 0$	2	5	2
$M_L = -1$	2	4	2
$M_L = -2$	1	3	1
$M_L = -3$	1	2	1
$M_L = -4$		1	

For $L = 4$, only the column $M_S = 0$ is used. It means that $S = 0$ and the spin multiplicity $2S + 1 = 1$, a singlet state, indicated by the term symbol ^1G

LS coupling - d^2 electronic configuration

Obtaining the *J* values

The total angular momentum *J* may have several values in the range

$$J = L+S, L+S-1, L+S-2, \ldots , |L-S|$$

As $L = 4$ and $S = 0$, the unique *J* value is 4, and the resulting term symbol is

$$^1G_4$$

LS coupling - d^2 electronic configuration

Removing the contribution of $^1G_4$ term from the central column

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 4$			
$M_L = 3$	1	1	1
$M_L = 2$	1	2	1
$M_L = 1$	2	3	2
$M_L = 0$	2	4	2
$M_L = -1$	2	3	2
$M_L = -2$	1	2	1
$M_L = -3$	1	1	1
$M_L = -4$			

All lines go from $M_L = 3$ until $M_L = -3$, indicating a value of $L = 3$, which corresponds to a F symbol.

LS coupling - d^2 electronic configuration

Extracting the term symbol

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 4$			
$M_L = 3$	1	1	1
$M_L = 2$	1	2	1
$M_L = 1$	2	3	2
$M_L = 0$	2	4	2
$M_L = -1$	2	3	2
$M_L = -2$	1	2	1
$M_L = -3$	1	1	1
$M_L = -4$			

All columns go from $M_S = 1$ until $M_S = -1$, indicating a value of $S = 1$, and the spin multiplicity $2S + 1 = 3$, a triplet state, indicated by the term symbol ^3F

LS coupling - d^2 electronic configuration

Obtaining the *J* values

$$J = L+S, L+S-1, L+S-2, \ldots, |L-S|$$

As $L = 3$ and $S = 1$, the J values are 4, 3, and 2, resulting in the term symbol

$$^3F_{4,3,2}$$

LS coupling - d^2 electronic configuration

Removing the contribution of $^3F_{4,3,2}$ term from all columns

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 4$			
$M_L = 3$			
$M_L = 2$		1	
$M_L = 1$	1	2	1
$M_L = 0$	1	3	1
$M_L = -1$	1	2	1
$M_L = -2$		1	
$M_L = -3$			
$M_L = -4$			

This is the same counting table obtained for the p^2 electronic configuration, which has the terms $^1D_2$, $^3P_{2,1,0}$, and $^1S_0$.

LS coupling - d^2 electronic configuration

Colecting all terms

$^1G_4$ $^3F_{4,3,2}$ $^1D_2$ $^3P_{2,1,0}$ $^1S_0$

LS coupling

Hund's rules

1) The term with the highest spin multiplicity is the lower energy term.

2) For electronic configurations less than half filled, the lower *J* has the lower energy.

3) When there are more than one term with the highest spin multiplicity, the term with the highest *L* value is the term with the lowest energy.

- As a result, the lowest energy term is the $^3F_2$ term.

LS coupling

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

spin multiplicity = 2S+1

	0	1	2	3	4	5	6	7	8	9	10	11 ...
ℓ (for electrons)	s	p	d	f	g	h	i	k	l	m	n	o ...
L (for atoms)	S	P	D	F	G	H	I	K	L	M	N	O...

j and J are intentionally missing

LS coupling

s^1	$^2S_{1/2}$
s^2	$^1S_0$
p^1, p^5	$^2P_{3/2,1/2}{}^o$
p^2, p^4	$^3P_{2,1,0}$ $^1D_2$ $^1S_0$
p^3	$^4S_{3/2}{}^o$ $^2D_{5/2,3/2}{}^o$ $^2P_{3/2,1/2}{}^o$
p^6	$^1S_0$
d^1, d^9	$^2D_{5/2,3/2}$
d^2, d^8	$^3F_{4,3,2}$ $^3P_{2,1,0}$ $^1G_4$ $^1D_2$ $^1S_0$
d^3, d^7	$^4F_{9/2,7/2,5/2,3/2}$ $^4P_{5/2,3/2,1/2}$ $^2H_{11/2,9/2}$ $^2G_{9/2,7/2}$ $^2F_{7/2,5/2}$ $^2D(2)_{5/2,3/2}$ $^2P_{3/2,1/2}$
d^4, d^6	$^5D_{4,3,2,1,0}$ $^3H_{6,5,4}$ $^3G_{5,4,3}$ $^3F(2)_{4,3,2}$ $^3D_{3,2,1}$ $^3P(2)_{2,1,0}$ $^1I_6$ $^1G(2)_4$ $^1F_3$ $^1D(2)_2$ $^1S(2)_0$
d^5	$^6S_{5/2}$ $^4G_{11/2,9/2,7/2,5/2}$ $^4F_{9/2,7/2,5/2,3/2}$ $^4D_{7/2,5/2,3/2,1/2}$ $^4P_{5/2,3/2,1/2}$ $^2I_{13/2,11/2}$ $^2H_{11/2,9/2}$ $^2G(2)_{9/2,7/2}$ $^2F(2)_{7/2,5/2}$ $^2D(3)_{5/2,3/2}$ $^2P_{3/2,1/2}$ $^2S_{1/2}$
d^{10}	$^1S_0$

LS coupling

f^1, f^{13}	$^2F^o$
f^2, f^{12}	^3H ^3F ^3P ^1I ^1G ^1D ^1S
f^3, f^{11}	$^4I^o$ $^4G^o$ $^4F^o$ $^4D^o$ $^4S^o$ $^2L^o$ $^2K^o$ $^2I^o$ $^2H^o(2)$ $^2G^o(2)$ $^2F^o(2)$ $^2D^o(2)$ $^2P^o$
f^4, f^{10}	^5I ^5G ^5F ^5D ^5S ^3M ^3L $^3K(2)$ $^3I(2)$ $^3H(4)$ $^3G(3)$ $^3F(4)$ $^3D(2)$ $^3P(3)$ ^1N $^1L(2)$ ^1K $^1I(3)$ $^1H(2)$ $^1G(4)$ ^1F $^1D(4)$ $^1S(2)$
f^5, f^9	$^6H^o$ $^6F^o$ $^6P^o$ $^4M^o$ $^4L^o$ $^4K^o(2)$ $^4I^o(3)$ $^4H^o(3)$ $^4G^o(4)$ $^4F^o(4)$ $^4D^o(3)$ $^4P^o(2)$ $^4S^o$ $^2O^o$ $^2N^o$ $^2M^o(2)$ $^2L^o(3)$ $^2K^o(5)$ $^2I^o(5)$ $^2H^o(7)$ $^2G^o(6)$ $^2F^o(7)$ $^2D^o(5)$ $^2P^o(4)$
f^6, f^8	^7F ^5L ^5K $^5I(2)$ $^5H(2)$ $^5G(3)$ $^5F(2)$ $^5D(3)$ ^5P ^5S ^3O ^3N $^3M(3)$ $^3L(3)$ $^3K(6)$ $^3I(6)$ $^3H(9)$ $^3G(7)$ $^3F(9)$ $^3D(5)$ $^3P(6)$ ^1Q $^1N(2)$ $^1M(2)$ $^1L(4)$ $^1K(3)$ $^1I(7)$ $^1H(4)$ $^1G(8)$ $^1F(4)$ $^1D(6)$ ^1P $^1S(4)$
f^7	$^8S^o$ $^6I^o$ $^6H^o$ $^6G^o$ $^6F^o$ $^6D^o$ $^6P^o$ $^4N^o$ $^4M^o$ $^4L^o(3)$ $^4K^o(3)$ $^4I^o(5)$ $^4H^o(5)$ $^4G^o(7)$ $^4F^o(5)$ $^4D^o(6)$ $^4P^o(2)$ $^4S^o(2)$ $^2Q^o$ $^2O^o$ $^2N^o(2)$ $^2M^o(4)$ $^2L^o(5)$ $^2K^o(7)$ $^2I^o(9)$ $^2H^o(9)$ $^2G^o(10)$ $^2F^o(10)$ $^2D^o(7)$ $^2P^o(5)$ $^2S^o(2)$
f^{14}	$^1S_0$

LS coupling

Parity indication

In the cases that the sum of ℓ values for all electrons is equal to an odd number, the term symbol is

$$^{2S+1}L_J^{\circ}$$

Examples

$p^1 \Rightarrow {}^2P^{\circ}_{3/2,1/2}$

$p^3 \Rightarrow {}^4S^{\circ}_{3/2} \quad {}^2D^{\circ}_{5/2,3/2} \quad {}^2P^{\circ}_{3/2,1/2}$

$f^1 \Rightarrow {}^2F^{\circ}_{7/2,5/2}$

LS coupling

Non equivalent electrons configurations.
The case s^1p^1 - building the microstates

s orbital	p orbitals				
$m_l = 0$	$m_l = 1$	$m_l = 0$ p_z	$m_l = -1$	$M_L = \sum m_l$	$M_S = \sum m_s$
x	x			1	1, 0, 0, -1
x		x		0	1, 0, 0, -1
x			x	-1	1, 0, 0, -1

LS coupling - s^1p^1 electronic configuration

Counting the microstates

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 1$	1	2	1
$M_L = 0$	1	2	1
$M_L = -1$	1	2	1

In all columns M_L spans from 1 to -1, indicating $L = 1$ and a term P

LS coupling - s^1p^1 electronic configuration

Extracting the terms

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 1$	1	2	1
$M_L = 0$	1	2	1
$M_L = -1$	1	2	1

If we consider all columns, M_S spans from 1 to -1, indicating an S value equal to 1, and $2S+1 = 3$, which results in a triplet state term ^3P

LS coupling - s^1p^1 electronic configuration

Obtaining the *J* values

$$J = L+S, L+S-1, L+S-2, \ldots , |L-S|$$

As $L = 1$ and $S = 1$, the J values are 2, 1, and 0, resulting in the term symbol

$$^3P^{\circ}_{2,1,0}$$

The parity symbol indicates that the sum of all ℓ is an odd number (s + p; 0 + 1 = 1).

LS coupling - s^1p^1 electronic configuration

Removing the contributions of the ^3P term from all columns

	$M_S = 1$	$M_S = 0$	$M_S = -1$
$M_L = 1$		1	
$M_L = 0$		1	
$M_L = -1$		1	

- In all columns M_L spans from 1 to -1, indicating $L = 1$ and a term P
- In the central column $M_S = 0$, indicating $S = 0$, $2S+1 = 1$, a singlet state, which results in the term ^1P

LS coupling - s^1p^1 electronic configuration

Obtaining the *J* values

$$J = L+S, L+S-1, L+S-2, \ldots, |L-S|$$

As $L = 1$ and $S = 0$, the unique J value is 1, resulting in the term symbol

$$^1P_1^\circ$$

The parity symbol indicates that the sum of all ℓ is an odd number (s + p; 0 + 1 = 1).

LS coupling - s^1d^1 electronic configuration

Colecting all terms

$^3P^\circ_{2,1,0}$ $^1P^\circ_1$

LS coupling - non equivalent electrons

$ns^1n's^1$	$^1S\ ^3S$
s^1p^1, s^1p^5	$^1P^o\ ^3P^o$
s^1d^1, s^1d^9	$^1D\ ^3D$
s^1f^1, s^1f^{13}	$^1F^o\ ^3F^o$
$np^1n'p^1$, $np^1n'p^5$, $np^5n'p^5$	$^1S\ ^1P\ ^1D\ ^3S\ ^3P\ ^3D$
p^1d^1, p^1d^9, p^5d^1, p^5d^9	$^1P^o\ ^1D^o\ ^1F^o\ ^3P^o\ ^3D^o\ ^3F^o$
p^1f^1, p^1f^{13}, p^5f^1, p^5f^{13}	$^1D\ ^1F\ ^1G\ ^3D\ ^3F\ ^3G$

- As the terms for $p^1 = p^5$ and $d^1 = d^9$, the terms for p^1d^1, p^1d^9, p^5d^1, and p^5d^9 are the same.

$nd^1n'd^1$, $nd^9n'd^1$, $nd^9n'd^9$	^1S ^1P ^1D ^1F ^1G ^3S ^3P ^3D ^3F ^3G
d^1f^1, d^1f^{13}, d^9f^1, d^9f^{13}	$^1P^o$ $^1D^o$ $^1F^o$ $^1G^o$ $^1H^o$ $^3P^o$ $^3D^o$ $^3F^o$ $^3G^o$ $^3H^o$
$nf^1n'f^1$, $nf^1n'f^{13}$	^1S ^1P ^1D ^1F ^1G ^1H ^1I ^3S ^3P ^3D ^3F ^3G ^3H ^3I
$ns^1n's^1n''s^1$	$^2S(2)$ ^4S
$ns^1n's^1p^1$, $ns^1n's^1p^5$	$^2P^o(2)$ $^4P^o$
$ns^1n's^1d^1$, $ns^1n's^1d^9$	$^2D(2)$ ^4D
$s^1np^1n'p^1$, $s^1np^1n'p^5$, $s^1np^5n'p^5$	$^2S(2)$ ^4S $^2P(2)$ ^4P $^2D(2)$ ^4D
$s^1p^1d^1$, $s^1p^5d^1$, $s^1p^1d^9$, $s^1p^5d^9$	$^2P^o(2)$ $^4P^o$ $^2D^o(2)$ $^4D^o$ $^2F^o(2)$ $^4F^o$
$np^1n'p^1n''p^1$, $np^1n'p^1n''p^5$, $np^1n'p^5n''p^5$, $np^5n'p^5n''p^5$	$^2S(2)$ ^4S $^2P(6)$ $^4P(3)$ $^2D(4)$ $^4D(2)$ $^2F(2)$ ^4F
$np^1n'p^1d^1$, $np^1n'p^5d^1$, $np^1n'p^1d^9$, $np^1n'p^5d^9$	$^2S(2)$ ^4S $^2P(4)$ $^4P(2)$ $^2D(6)$ $^4D(3)$ $^2F(4)$ $^4F(2)$ $^2G(2)$ ^4G
s^1p^2	$^4P_{5/2,3/2,1/2}$ $^2D_{5/2,3/2}$ $^2P_{3/2,1/2}$ $^3S_{1/2}$
s^1p^3	$^5S_2^o$ $^3D_{3,2,1}^o$ $^3P_{2,1,0}^o$ $^3S_1^o$ $^1D_2^o$ $^1P_1^o$
s^1d^2, s^1d^8	^4F ^4P ^2G ^2F ^2D ^2P ^2S

LS coupling - application to determine the electronic configuration

- The ground state of Cu, Ag, and Au is a singlet. Determine the electronic configuration of these elements.

Cu possible electronic configurations are

$4s^2\ 3d^9$ $^2D_{5/2,3/2}$

$4s^1\ 3d^{10}$ $^2S_{1/2}$ (singlet; it is a false dublet)

$4s^0\ 3d^{10}\ 4p^1$ $^2P^o_{3/2,1/2}$

As a conclusion, the electronic configuration for Cu is $4s^1\ 3d^{10}$. Similarly, the electronic configurations for Ag and Au are $5s^1\ 4d^{10}$ and $6s^1\ 5d^{10}$, respectively.

LS coupling - application to determine the electronic configurations

- Ground state terms

$$Ni = {}^3F_4 \quad Pd = {}^1S_0 \quad Pt = {}^3D_3$$

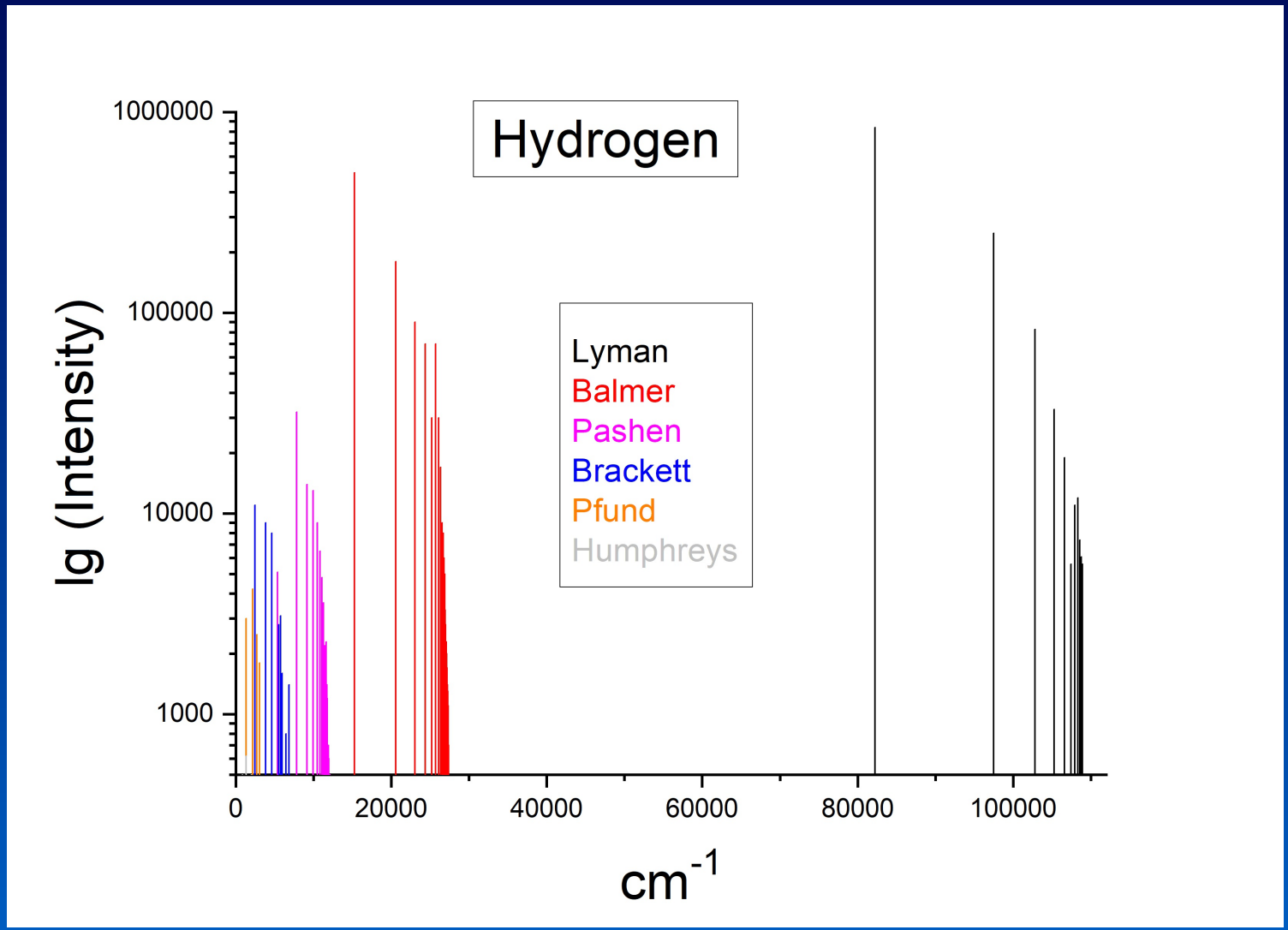
Possible electronic configurations and terms

$s^2\ d^8$	${}^3F_{4,3,2}$	${}^3P_{2,1,0}$	${}^1G_4$	${}^1D_2$	${}^1S_0$	
$s^1\ d^9$	${}^3D_{3,2,1}$	${}^1D_2$				
$s^0\ d^{10}$	${}^1S_0$					

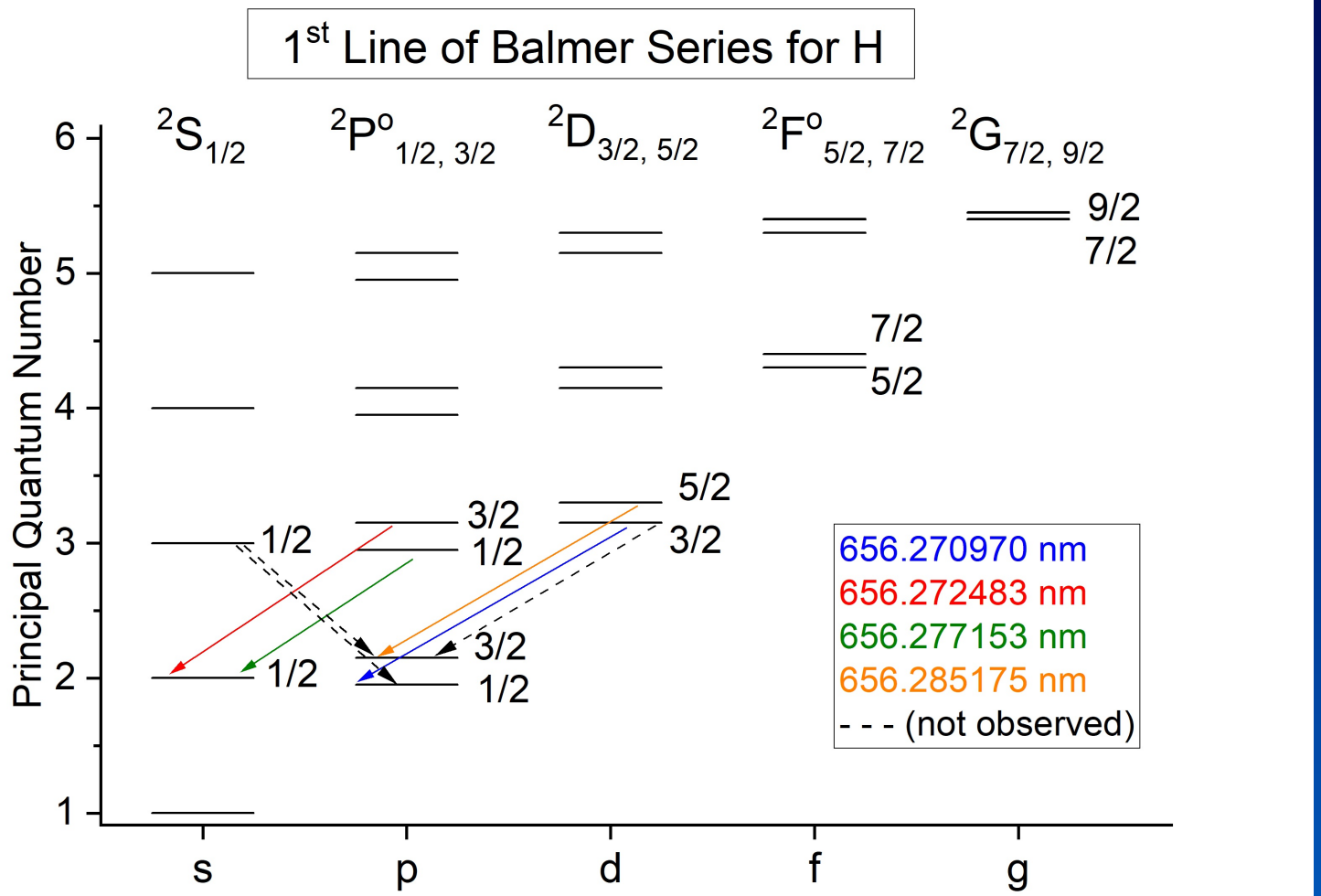
As a conclusion, the electronic configurations are

$$Ni = 4s^2\ 3d^8 \quad Pd = 5s^0\ 4d^{10} \quad Pt = 6s^1\ 5d^9$$

LS coupling - application to label electronic transitions



LS coupling - application to label electronic transitions



Selection Rules
Electric dipole allowed electronic transitions

LS coupling

$T \leftrightarrow T^{\circ}$

$\Delta S = 0$

$\Delta L = 0, \pm 1$

$\Delta J = 0, \pm 1$ ($0 \leftrightarrow 0$ forbiden)

LS coupling - application to label electronic transitions