

Nel caso di shell complete, ho una sola possibilità di distribuire gli elettroni negli spin-orbitali e la funzione d'onda sarà un unico determinante di Slater.

$$\psi(1,2, \dots 2N) = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \psi_1\alpha(1) & \psi_1\beta(1) & \dots & \psi_N\alpha(1) & \psi_N\beta(1) \\ \psi_1\alpha(2) & \psi_1\beta(2) & \dots & \psi_N\alpha(2) & \psi_N\beta(2) \\ \vdots & \vdots & \dots & \vdots & \vdots \\ \psi_1\alpha(2N) & \psi_1\beta(2N) & \dots & \psi_N\alpha(2N) & \psi_N\beta(2N) \end{vmatrix}$$

Per un atomo con $2N$ elettroni l'hamiltoniana è:

$$H = -\frac{1}{2} \sum_{j=1}^{2N} \nabla_j^2 - \sum_{j=1}^{2N} \frac{Z}{r_j} + \sum_{j=1}^{2N} \sum_{j>i} \frac{1}{r_{ij}}$$
$$= \sum_{j=1}^{2N} H_j + \sum_{j=1}^{2N} \sum_{j>i} \frac{1}{r_{ij}}$$

$$E = \langle \psi(1,2, \dots 2N) | H | \psi(1,2, \dots 2N) \rangle$$

$$E = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N (2J_{ij} - K_{ij})$$

$$I_j = \langle \psi_j | H_j | \psi_j \rangle$$

$$= \int d\mathbf{r} \psi_j^*(\mathbf{r}) H_j \psi_j(\mathbf{r})$$

$$E = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N (2J_{ij} - K_{ij})$$

$$J_{ij} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2)$$

integrali di Coulomb

$$E = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N (2J_{ij} - K_{ij})$$

$$K_{ij} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_1)$$

integrali di scambio

Per He: $E = 2I_1 + 2J_{11} - K_{11}$

Ma $K_{11} = J_{11} \Rightarrow E_{\text{He}} = 2I_1 + 2J_{11} - J_{11} = 2I_1 + J_{11}$

$$\hat{F}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \varepsilon_i\psi_i(\mathbf{r}_1) \quad i = 1, 2, \dots, N \quad \text{Equazioni di Hartree Fock}$$

$$\hat{F}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_{j=1}^N 2\hat{J}_j(\mathbf{r}_1) - \hat{K}_j(\mathbf{r}_1) \quad \text{Operatore di Fock}$$

$$\hat{h}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}$$

$$\hat{J}_j(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \psi_i(\mathbf{r}_1) \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_2)$$

$$\hat{K}_j(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \psi_j(\mathbf{r}_1) \int d\mathbf{r}_2 \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2)$$

Metodo Self Consistent Field

Come per l'elio:

1. Si sceglie funzione di prova

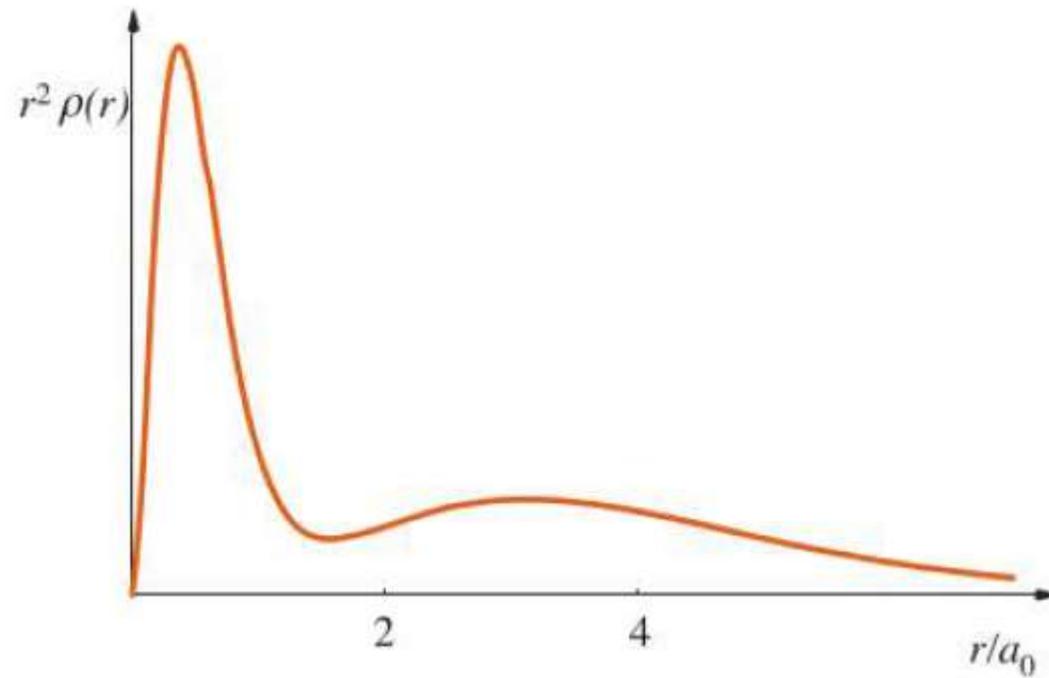
$$\psi(1,2, \dots, 2N) = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \psi_1\alpha(1) & \psi_1\beta(1) & \dots & \psi_N\alpha(1) & \psi_N\beta(1) \\ \psi_1\alpha(2) & \psi_1\beta(2) & \dots & \psi_N\alpha(2) & \psi_N\beta(2) \\ \vdots & \vdots & \dots & \vdots & \vdots \\ \psi_1\alpha(2N) & \psi_1\beta(2N) & \dots & \psi_N\alpha(2N) & \psi_N\beta(2N) \end{vmatrix}$$

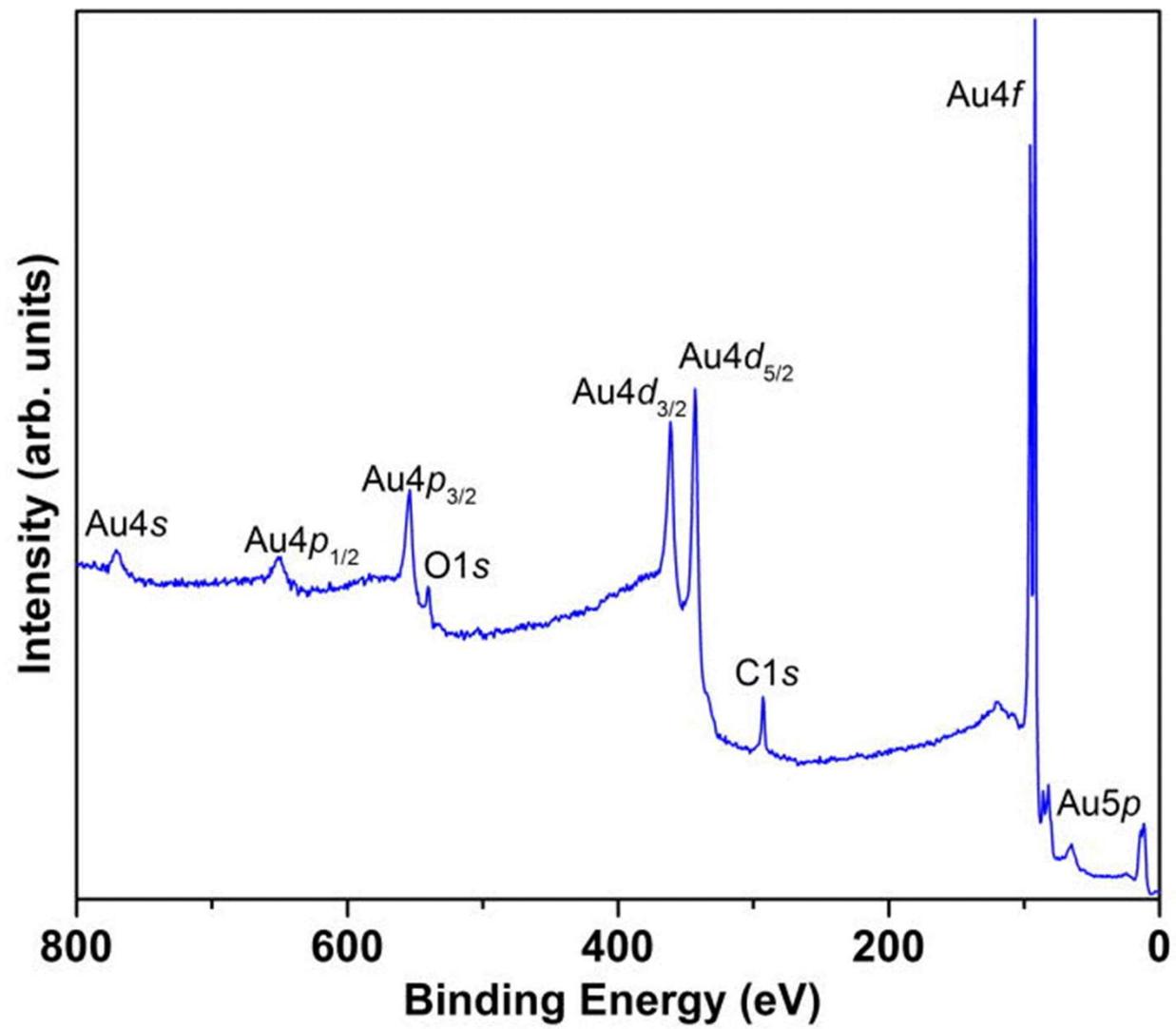
2. Si trovano autovalori e autovettori soluzioni delle equazioni di HF

$$\hat{F}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \varepsilon_i\psi_i(\mathbf{r}_1) \quad i = 1, 2, \dots, N$$

3. Si scrive la nuova funzione di prova e si ripete finchè non si minimizza l'energia totale E

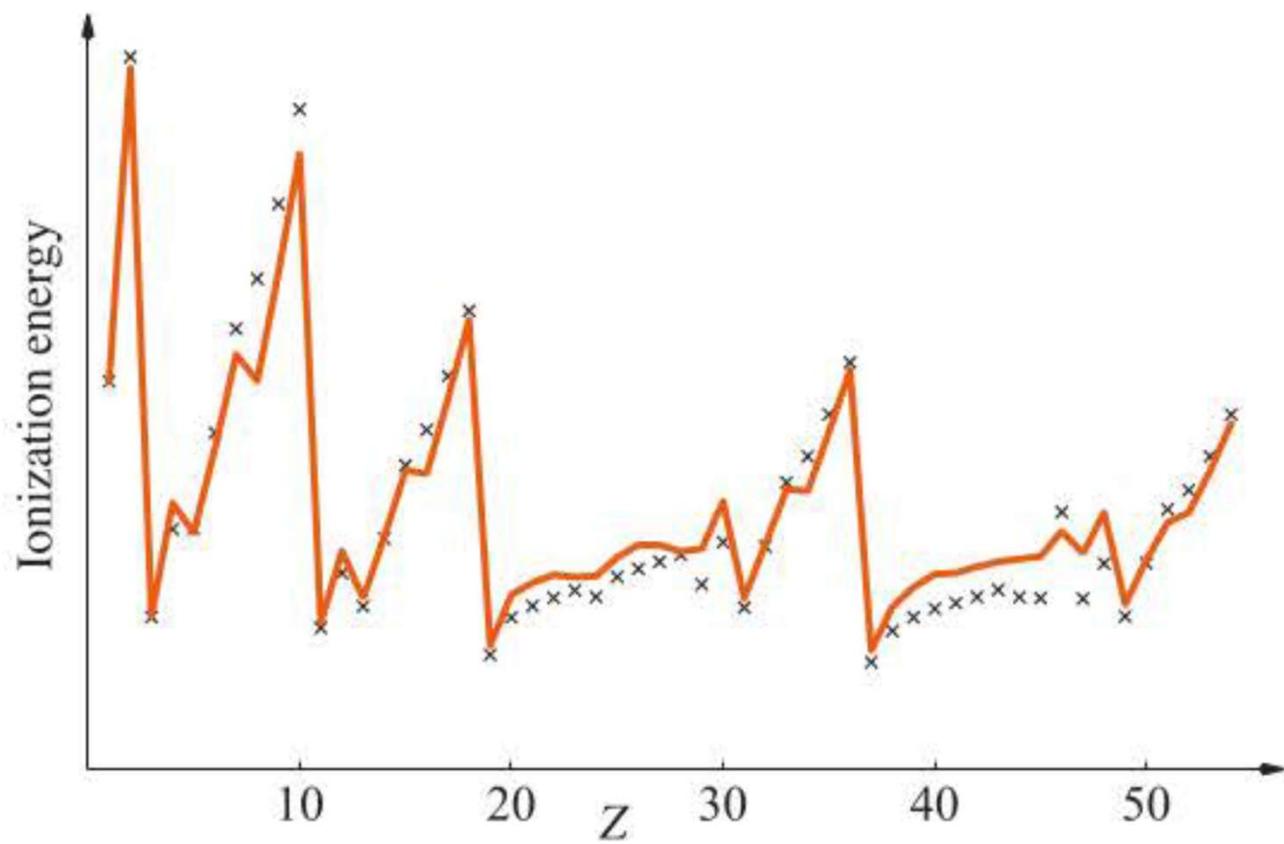
Il metodo HF fornisce la densità elettronica in cui si possono riconoscere le diverse shell. Ad esempio per il litio ($N=3$), si vedono due massimi corrispondenti alle shell 1 e 2





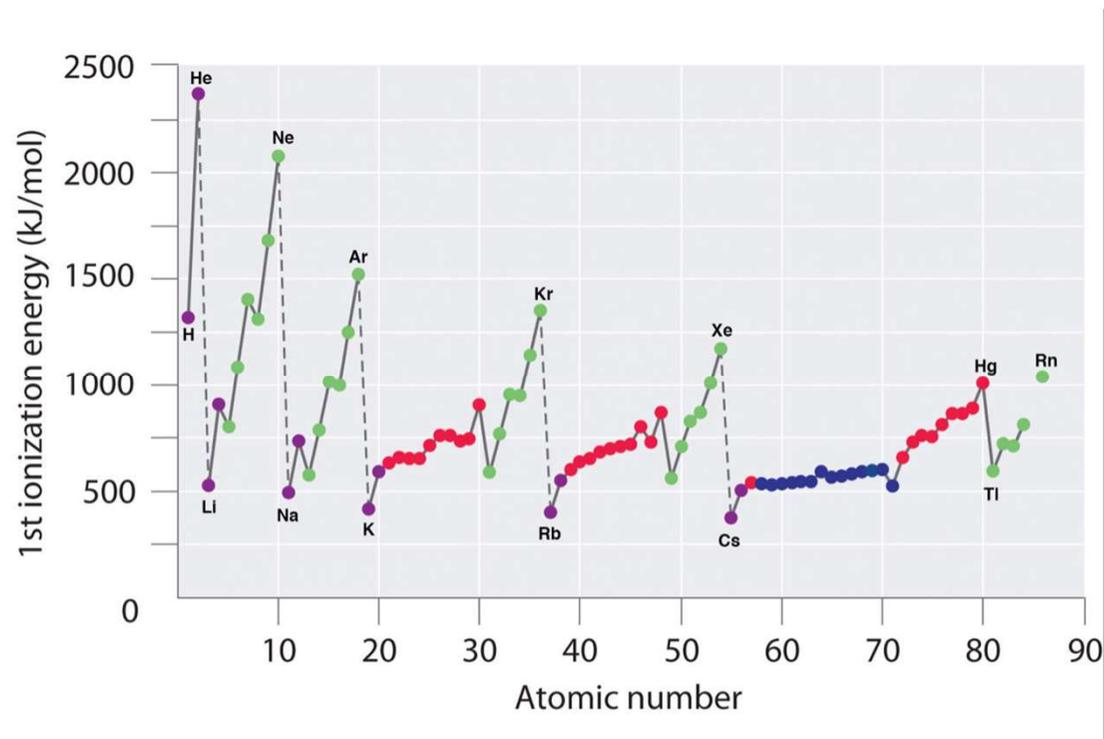
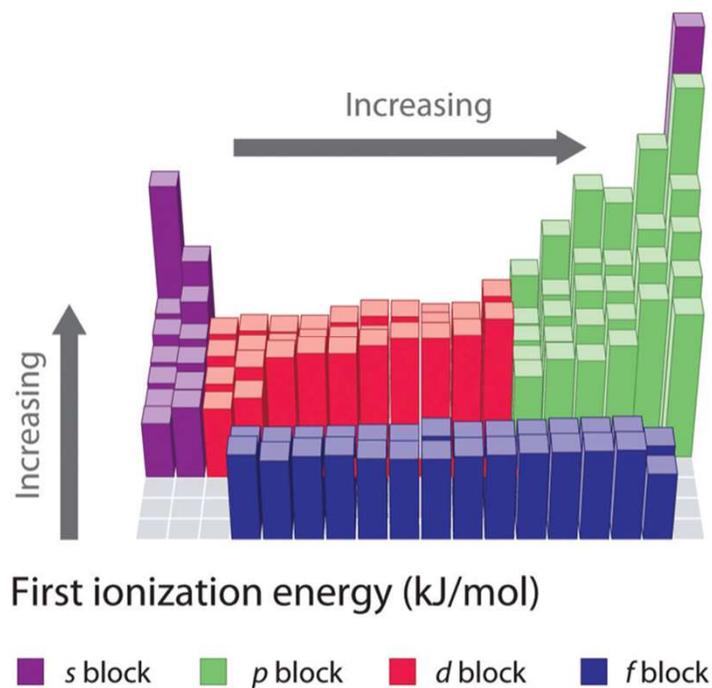
Gli autovalori dello stato fondamentale delle equazioni di HF sono le energie di ionizzazione dei rispettivi livelli (Koopmans)

Electron removed	Resulting orbital occupancy	Ionization energies/MJ·mol ⁻¹		
		Koopmans's approximation	Direct Hartree-Fock calculation	Experimental
<i>Neon</i>				
1s	1s2s ² 2p ⁶	86.0	83.80	83.96
2s	1s ² 2s2p ⁶	5.07	4.76	4.68
2p	1s ² 2s ² 2p ⁵	2.23	1.92	2.08
<i>Argon</i>				
1s	1s2s ² 2p ⁶ 3s ² 3p ⁶	311.4	308.25	309.32
2s	1s ² 2s2p ⁶ 3s ² 3p ⁶	32.35	31.33	
2p	1s ² 2s ² 2p ⁵ 3s ² 3p ⁶	25.13	24.01	23.97
3s	1s ² 2s ² 2p ⁶ 3s3p ⁶	3.35	3.20	2.82
3p	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	1.55	1.43	1.52



— Experimental data

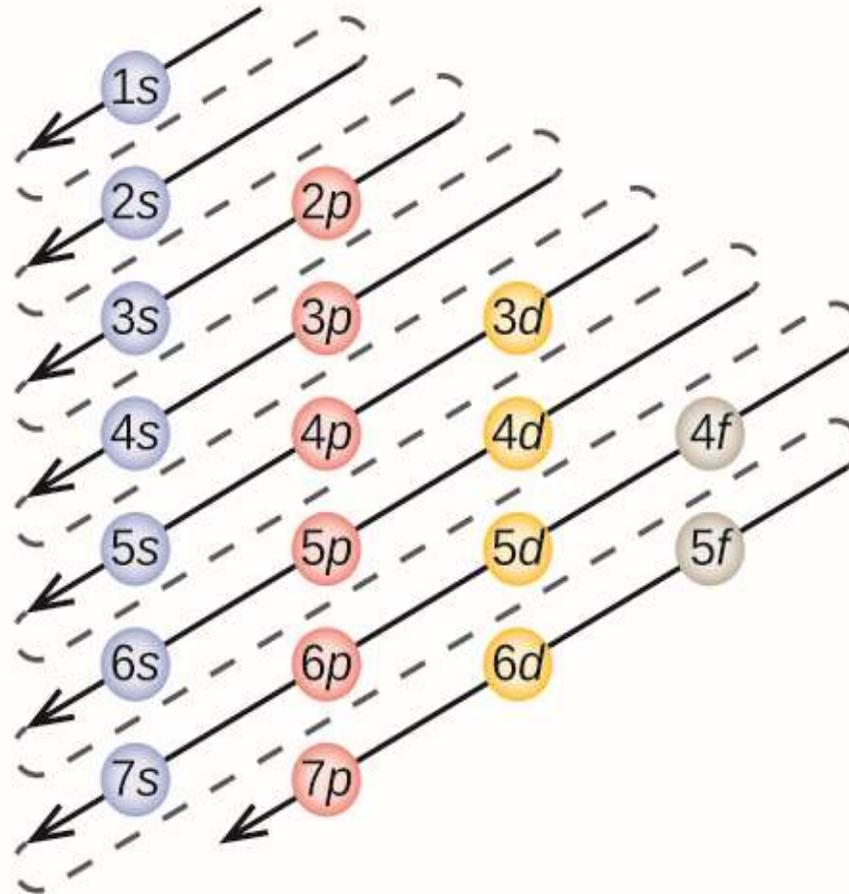
× HF



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Aufbau: regola di Madelung



Eccezioni all'Aufbau nei metalli di transizione

Element	Symbol	Atomic number	Aufbau's prediction	Experimental observed
Chromium	Cr	24	$[\text{Ar}] 4s^2 3d^4$	$[\text{Ar}] 4s^1 3d^5$
Copper	Cu	29	$[\text{Ar}] 4s^2 3d^9$	$[\text{Ar}] 4s^1 3d^{10}$
Niobium	Nb	41	$[\text{Kr}] 5s^2 4d^3$	$[\text{Kr}] 5s^1 4d^4$
Molybdenum	Mo	42	$[\text{Kr}] 5s^2 4d^4$	$[\text{Kr}] 5s^1 4d^5$
Ruthenium	Ru	44	$[\text{Kr}] 5s^2 4d^6$	$[\text{Kr}] 5s^1 4d^7$
Rhodium	Rh	45	$[\text{Kr}] 5s^2 4d^7$	$[\text{Kr}] 5s^1 4d^8$
Palladium	Pd	46	$[\text{Kr}] 5s^2 4d^8$	$[\text{Kr}] 4d^{10}$
Silver	Ag	47	$[\text{Kr}] 5s^2 4d^9$	$[\text{Kr}] 5s^1 4d^{10}$
Platinum	Pt	78	$[\text{Xe}] 6s^2 4f^{14} 5d^8$	$[\text{Xe}] 6s^1 4f^{14} 5d^9$
Gold	Au	79	$[\text{Xe}] 6s^2 4f^{14} 5d^9$	$[\text{Xe}] 6s^1 4f^{14} 5d^{10}$

Eccezioni all'Aufbau nei lantanidi e attinidi

Element	Symbol	Atomic number	Aufbau's prediction	Experimentally observed
Lanthanum	La	57	$[\text{Xe}] 6s^2 4f^1$	$[\text{Xe}] 6s^2 5d^1$
Cerium	Ce	58	$[\text{Xe}] 6s^2 4f^2$	$[\text{Xe}] 6s^2 4f^1 5d^1$
Gadolinium	Gd	64	$[\text{Xe}] 6s^2 4f^8$	$[\text{Xe}] 6s^2 4f^7 5d^1$
Actinium	Ac	89	$[\text{Rn}] 7s^2 5f^1$	$[\text{Rn}] 7s^2 6d^1$
Thorium	Th	90	$[\text{Rn}] 7s^2 5f^2$	$[\text{Rn}] 7s^2 6d^2$
Protactinium	Pa	91	$[\text{Rn}] 7s^2 5f^3$	$[\text{Rn}] 7s^2 5f^2 6d^1$
Uranium	U	92	$[\text{Rn}] 7s^2 5f^4$	$[\text{Rn}] 7s^2 5f^3 6d^1$
Neptunium	Np	93	$[\text{Rn}] 7s^2 5f^5$	$[\text{Rn}] 7s^2 5f^4 6d^1$
Curium	Cm	96	$[\text{Rn}] 7s^2 5f^8$	$[\text{Rn}] 7s^2 5f^7 6d^1$
Lawrencium	Lr	103	$[\text{Rn}] 7s^2 5f^{14} 6d^1$	$[\text{Rn}] 7s^2 5f^{14} 7p^1$

Termine spettroscopico e regole di Hund

Nel caso di atomi a shell o sub-shell complete, determinare il termine spettroscopico è semplice.

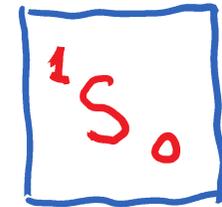
Esempio: gas nobili

$$L_z = \sum l_z = 0 \quad (\text{per ogni elettrone con } m_l, \text{ c'è un elettrone con } -m_l)$$

$$S_z = \sum s_z = 0 \quad (\text{per ogni } \uparrow \text{ c'è } \downarrow)$$

$$\Rightarrow \vec{L} = 0, \vec{S} = 0, \vec{J} = \vec{L} + \vec{S} = 0$$

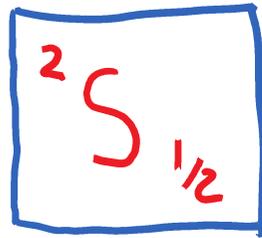
\Rightarrow



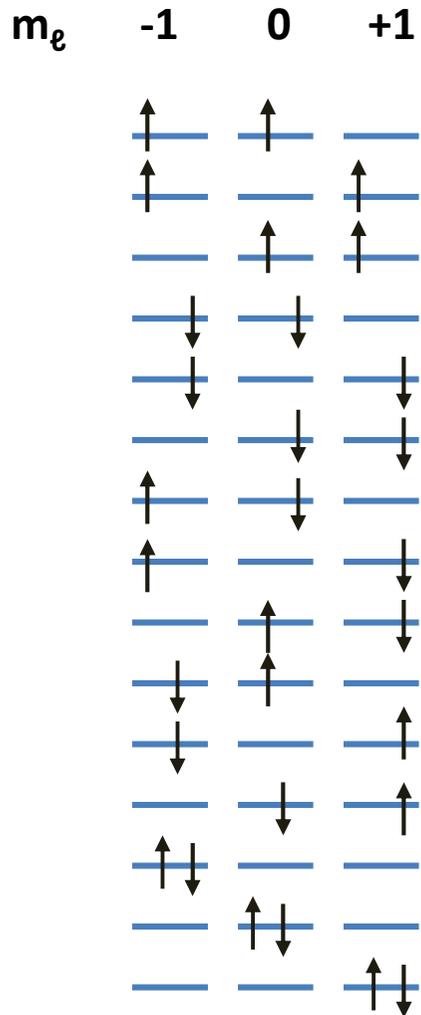
Esempio: metalli alcalini

Rispetto alla configurazione elettronica di un gas nobile
c'è un elettrone in più in un orbitale ns

$$\Rightarrow \begin{array}{l} S = \frac{1}{2} \\ L = 0 \end{array} \begin{array}{l} \text{gas nobile} \\ (0 + \frac{1}{2}) \\ (0 + 0) \end{array} \Rightarrow J = \frac{1}{2} \begin{array}{l} (|l+s|, \dots, |l-s|) \\ (\frac{1}{2} \dots \frac{1}{2}) \end{array}$$



Termini spettroscopico del Carbonio



1. Individuo le possibilità con cui i due elettroni 2p possono essere messi negli spin-orbitali rispettando il principio di esclusione di Pauli

Nota: le possibilità per mettere N elettroni in G spin-orbitali sono:

$$\frac{G!}{N!(G-N)!}$$

Nel caso del carbonio, sono 15

m_e	-1	0	+1	L_z	S_z	J_z
				m_L	m_S	m_J
	↑	↑	—	-1	+1	0
	↑	—	↑	0	+1	+1
	—	↑	↑	+1	+1	+2
	↓	↓	—	-1	-1	-2
	↓	—	↓	0	-1	-1
	—	↓	↓	+1	-1	0
	↑	↓	—	-1	0	-1
	↑	—	↓	0	0	0
	—	↑	↓	+1	0	+1
	↓	↑	—	-1	0	-1
	↓	—	↑	0	0	0
	—	↓	↑	+1	0	+1
	↑↓	—	—	-2	0	-2
	—	↑↓	—	0	0	0
	—	—	↑↓	2	0	2

2. Calcolo la componente z di L, S, J

m_e	-1	0	+1	Lz	Sz	Jz
				m_L	m_S	m_J
	↑	↑	—	-1	+1	0
	↑	—	↑	0	+1	+1
	—	↑	↑	+1	+1	+2
	↓	↓	—	-1	-1	-2
	↓	—	↓	0	-1	-1
	—	↓	↓	+1	-1	0
	↑	↓	—	-1	0	-1
	↑	—	↓	0	0	0
	—	↑	↓	+1	0	+1
	↓	↑	—	-1	0	-1
	↓	—	↑	0	0	0
	—	↓	↑	+1	0	+1
	↑↓	—	—	-2	0	-2
	—	↑↓	—	0	0	0
	—	—	↑↓	2	0	2

3. Individuo gruppi di microstati corrispondenti a L più elevato

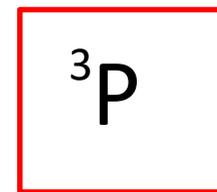
Ho uno stato con L=2 e S=0:

$1D_2$

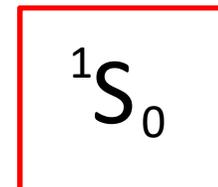
m_e	-1	0	+1	L_z	S_z	J_z
				m_L	m_S	m_J
	↑	↑		-1	+1	0
	↑		↑	0	+1	+1
		↑	↑	+1	+1	+2
	↓	↓		-1	-1	-2
	↓		↓	0	-1	-1
		↓	↓	+1	-1	0
	↑	↓		-1	0	-1
	↑		↓	0	0	0
		↑	↓	+1	0	+1
	↓	↑				
	↓		↑	0	0	0
		↓	↑			
	↑↓					
		↑↓				
			↑↓			

4. Procedo con i microstati restanti cercando L più elevato

Abbiamo stati con $L_z = -1, 0, 1$ che compaiono tutti con $S_z = -1, 0, 1$

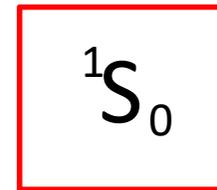
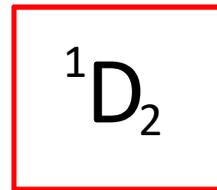


Lo stato rimanente è



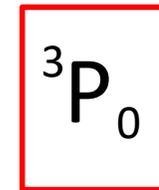
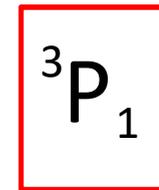
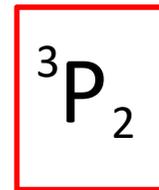
m_e	-1	0	+1	L_z	S_z	J_z
				m_L	m_S	m_J
	↑	↑	—	-1	+1	0
	↑	—	↑	0	+1	+1
	—	↑	↑	+1	+1	+2
	↓	↓	—	-1	-1	-2
	↓	—	↓	0	-1	-1
	—	↓	↓	+1	-1	0
	↑	↓	—	-1	0	-1
	↑	—	↓	0	0	0
	—	↑	↓	+1	0	+1
	↓	↑	—			
	↓	—	↑			
	—	↓	↑			
	↑↓	—	—			
	—	↑↓	—			
	—	—	↑↓			

5. Determino i possibili valori di J

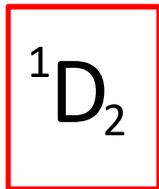


$J=2,1,0$

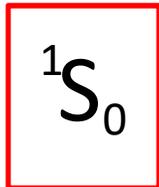
(somma di $L=1$ e $S=1$)



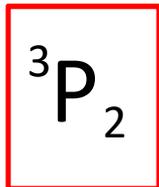
6. Controllo che il numero totale di stati sia conservato....dalla combinazione di N stati devo ottenere N stati



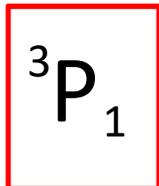
5 stati



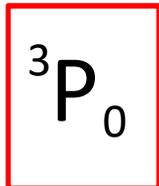
1 stato



5 stati



3 stati



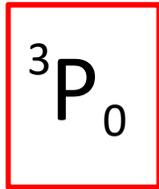
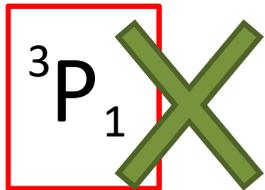
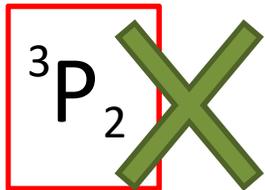
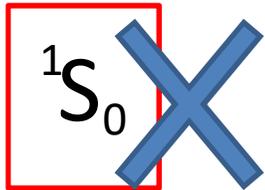
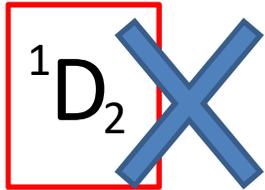
1 stato

Ogni termine spettroscopico ha $2J+1$ stati

Totale: 15 stati



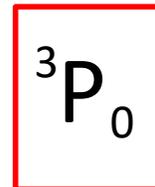
6. Determino lo stato fondamentale con la regola di Hund



1. Stato con S maggiore

2. Stato con L maggiore

3. Stato con J minore se subshell occupata per metà o meno



Ciò che abbiamo fatto è stato di individuare i possibili modi di combinare stati di singolo elettrone

in combinazioni $|l m_l s m_s\rangle$ e \vec{L} e \vec{S} definiti, o meglio, di stabilire i possibili \vec{L} e \vec{S} ottenibili.

Poi, abbiamo determinato \vec{J} come $\vec{J} = \vec{L} + \vec{S}$

Questa procedura è nota come

Accoppiamento $\vec{L}\vec{S}$ o di Russell-Saunders

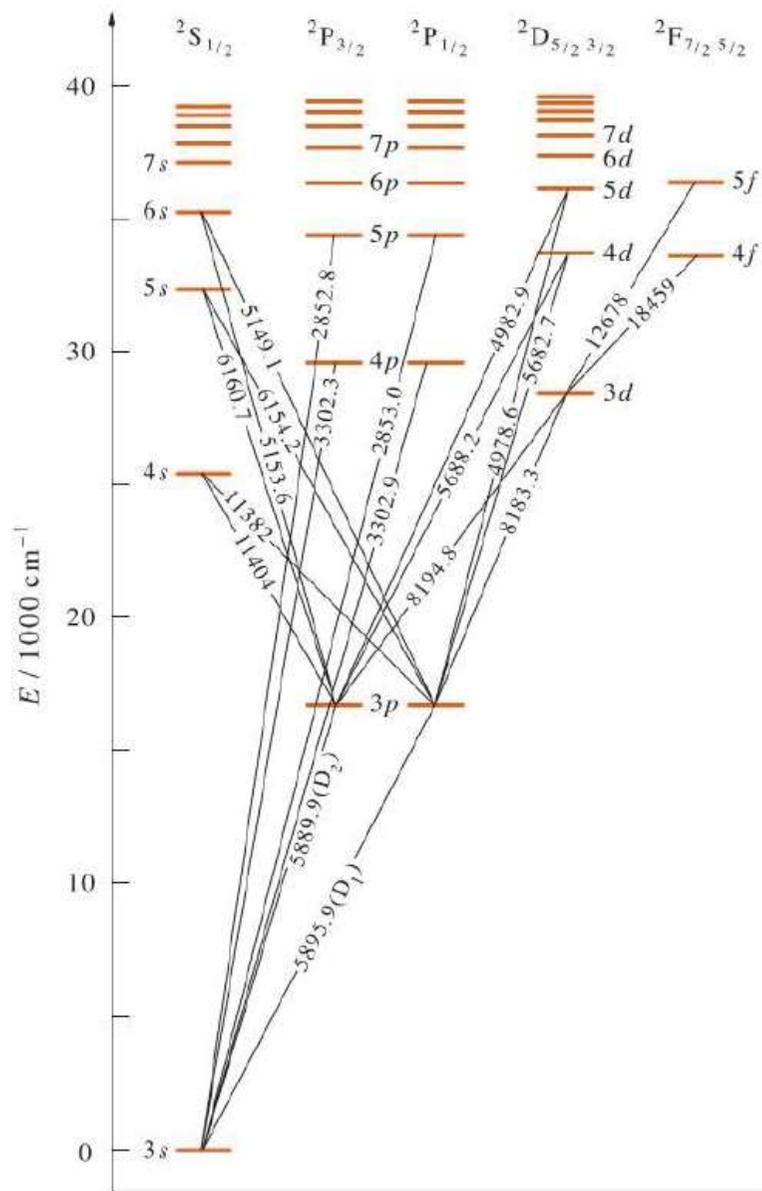


FIGURE 9.9
An energy-level diagram of atomic sodium.

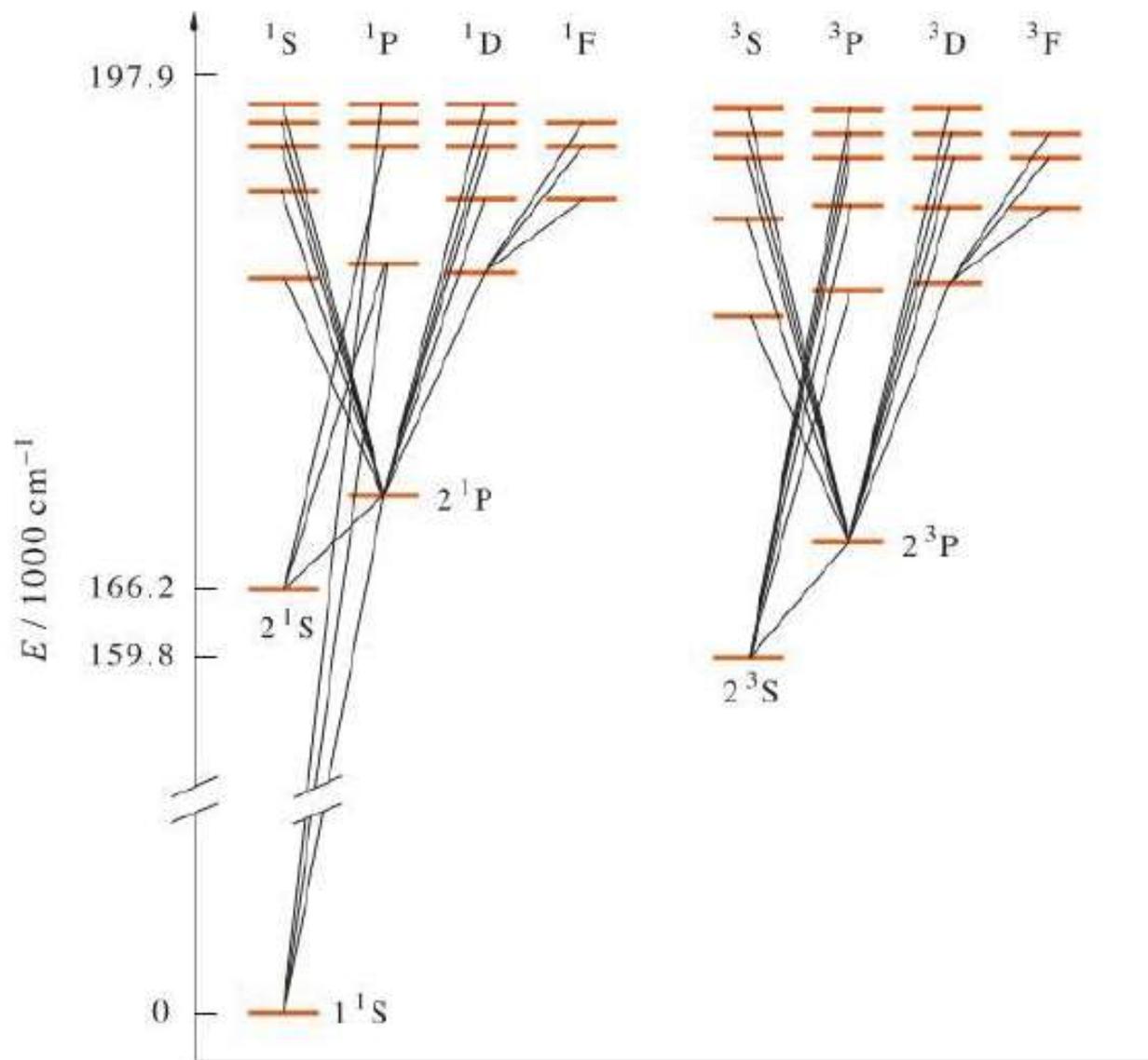


FIGURE 9.10

The energy-level diagram of a helium atom, showing the two separate sets of singlet and triplet states.

LS (Russell-Saunders) vs jj coupling

Per $Z > 35$, l'accoppiamento spin-orbita non è più trattabile come solo una perturbazione. I singoli elettroni vanno visti come particelle con j definito e non con l e s definiti...

