TEMA 3

El model de camp central

Sumari

- Introducció al camp central
- La taula periòdica
- Evidències espectroscòpiques

Bibliografia

- Woodgate, capítol 6
- Bransden-Joachain, cap. X.

El camp central (introducció)

Estructura per a *N* electrons

$$\left\{ \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} \right) + \sum_{i>j=1}^{N} \frac{e^2}{r_{ij}} \right\} \Psi(1,2,\ldots,N) = E\,\Psi(1,2,\ldots,N)$$

Volem un model a 1 cos (e independents)
La repulsió e-e és important
En separarem una part

$$\sum_{i>j=1}^{N} \frac{e^2}{r_{ij}} \approx \sum_{i=1}^{N} V_{ee}^{(1)}(r_i) + \sum_{i>j=1}^{N} V_{ee}^{(2)}(r_{ij})$$

El camp central

$$U(r) \equiv -\frac{Ze^2}{r} + V_{ee}^{(1)}(r)$$

Un model d'*electrons independents*

$$\left\{ \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m}\nabla_i^2 + U(r_i) \right) \right\} \Psi(1,2,\ldots,N) = E\,\Psi(1,2,\ldots,N)$$

Hamiltonians $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$

$$\mathcal{H}_0 = \sum_{i=1}^{N} \overbrace{\left(-\frac{\hbar^2}{2m}\nabla_i^2 \overbrace{- \frac{Ze^2}{r_i} + V_{ee}^{(1)}(r_i)}^{U(r_i)} \right)}^{h_0(i)}$$

$$\mathcal{H}_1 = \sum_{i>j=1}^{N} V_{ee}^{(2)}(r_{ij})$$

Descomposició necessària per al tractament pertorbatiu

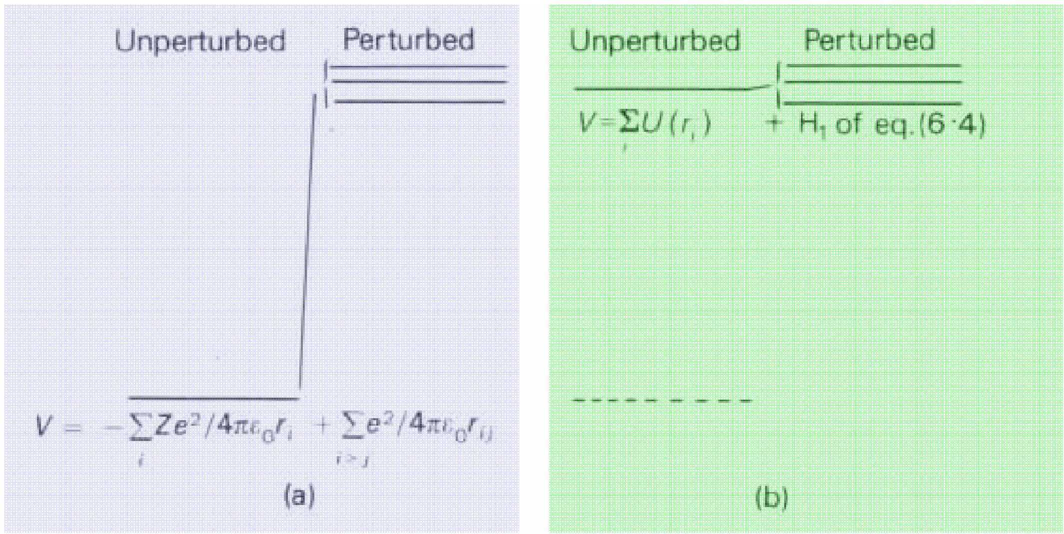


Fig. 6.1. Schematic energy level diagram, contrasting the use of (a) $-\sum_i Ze^2/4\pi\varepsilon_0 r_i$ and (b) $\sum_i U(r)$ as zeroth-order potentials.

Model d'electrons independents

$$\mathcal{H}_0 \Psi(1,2,\ldots,N) = E\,\Psi(1,2,\ldots,N)$$

$$\mathcal{H}_0 = \sum_{i=1}^{N} h_0(i)$$

$$\left\{ \begin{array}{l} h_0(i)\,\psi_i(\mathbf{r}_i\eta_i) = \varepsilon_i\,\psi_i(\mathbf{r}_i\eta_i) \\ \Psi(\mathbf{r}_1\eta_1, \mathbf{r}_2\eta_2, \ldots) = \prod_{i=1}^{N} \psi_i(\mathbf{r}_i\eta_i) \\ E = \sum_{i=1}^{N} \varepsilon_i \end{array} \right.$$

Orbitals monoelectrònics

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + U(r_i)\right)\psi_i(\mathbf{r}_i\eta_i) = \varepsilon_i\,\psi_i(\mathbf{r}_i\eta_i)$$

$$\varepsilon_i \equiv \varepsilon_{n_i\ell_i}$$

$$\psi_i(\mathbf{r}_i\eta_i) \equiv \psi_{n_i\ell_i m_{\ell i} m_{si}}(\mathbf{r}_i\eta_i) = R_{n_i\ell_i}(r_i)\,Y_{\ell_i m_{\ell i}}(\theta_i\phi_i)\,\chi_{m_{si}}(\eta_i)$$

Principi d'exclusió de Heisenberg: un electró a cada orbital $(n\ell m_\ell m_s)$

Una **capa** $n\ell$ té energia $\varepsilon_{n\ell}$

ℓ	s	p	d	f
Notació	0	1	2	3
Degeneració	2	6	10	14

Una **configuració** $\{n_1\ell_1, n_2\ell_2, \ldots n_N\ell_N\}$ té energia total $E = \sum_{i=1}^{N} \varepsilon_{n_i\ell_i}$

Diverses receptes per construir el camp central

average

$$U(r_k) \equiv -\frac{Ze^2}{r_k} + \overline{\sum_{i\neq k} \int d^3 r_i \, \frac{e^2 |\psi_i(r_i)|^2}{r_{ik}}}$$

Minimització de l'energia total

Principi d'exclusió de Pauli

Autoconsistència per iteracions

$$\cdots$$

$$\downarrow$$

$$\left\{\psi_i^{(I)}, i = 1, \ldots, N\right\}$$ Iteració *I*

$$\downarrow$$

$$U^{(I)}(r) = U[\psi_i^{(I)}](r)$$

$$\downarrow$$

$$\left\{\psi_i^{(I+1)}, i = 1, \ldots, N\right\}$$ Iteració *I+1*

$$\downarrow$$

$$U^{(I+1)}(r) = U[\psi_i^{(I+1)}](r)$$

$$\downarrow$$

$$\cdots$$

Models: Hartree, Hartree-Fock, Thomas-Fermi

La taula periòdica

El camp central *U(r)* té propietats comunes a tots els àtoms

Seqüència energètica de nivells monolelectrònics: $n+\ell$ creixent

$$\begin{array}{ccccc} 1s & & & & \\ 2s & 2p & & & \\ 3s & 3p & 3d & & \\ 4s & 4p & 4d & 4f & \\ 5s & 5p & 5d & 5f & 5g \\ 6s & 6p & 6d & \dots & \\ 7s & \dots & & & \end{array}$$

Nivells molt junts poden alternar-se

Exemple

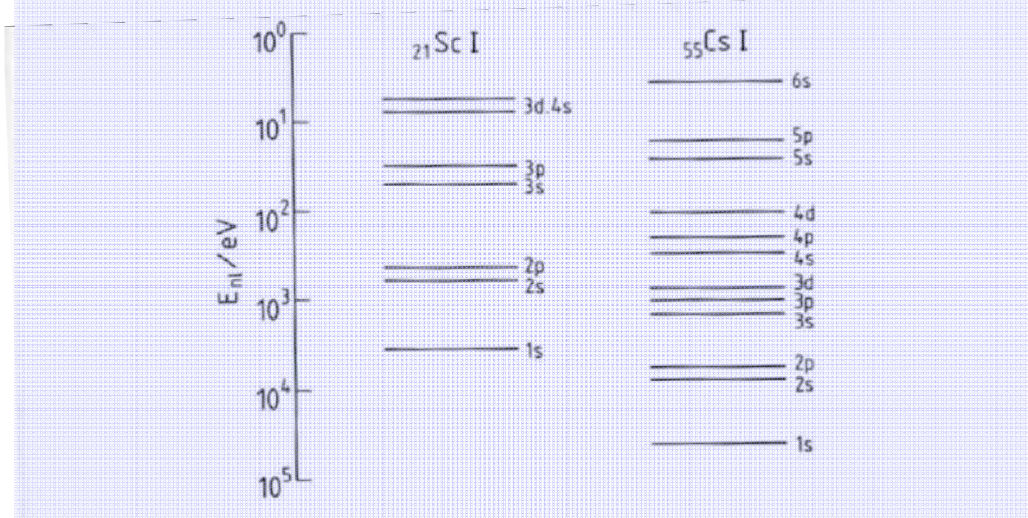
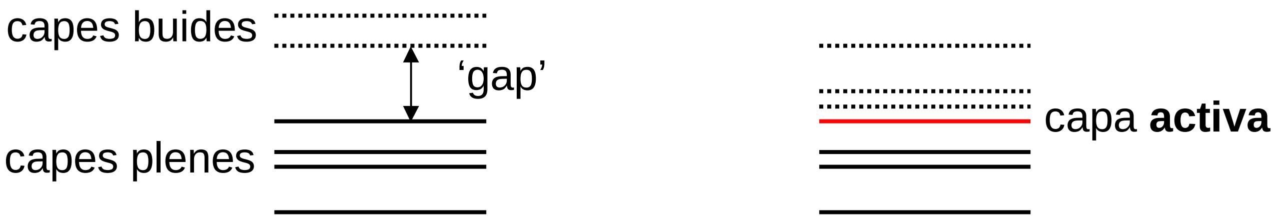


Fig. 5.1. Comparison of levels of Sc I ($Z=21$) and Cs I ($Z=55$). Note the logarithmic energy scale. (After ZI 76).

Capes plenes major estabilitat (reactivitat)



Electrons de **valència** i electrons **interns** (o de *core*)

Gasos nobles inerts: configuració $\ldots \mathrm{s}^2\mathrm{p}^6$

Configuracións semblants implica propietats químiques semblants

Gasos nobles, alcalins, halògens, …

La taula periòdica (Mendeleiev)

Periodic Table of Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Legend - click to find out more...

H - gas | Li - solid | Br - liquid | Tc - synthetic

Non-Metals	Transition Metals	Rare Earth Metals	Halogens
Alkali Metals	Alkali Earth Metals	Other Metals	Inert Elements

Appendix D

The ground levels and their electron configurations for neutral atoms. (The number of electrons in each shell is specified in the table.)

Z \ nl	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	...	Ground level
1 H	1											$^2S_{1/2}$
2 He	2											$^1S_0$
3 Li		1										$^2S_{1/2}$
4 Be		2										$^1S_0$
5 B		2	1									$^2P_{1/2}$
6 C	full	2	2									$^3P_0$
7 N		2	3									$^4S_{3/2}$
8 O		2	4									$^3P_2$
9 F		2	5									$^2P_{3/2}$
10 Ne		2	6									$^1S_0$
11 Na				1								$^2S_{1/2}$
12 Mg				2								$^1S_0$
13 Al				2	1							$^2P_{1/2}$
14 Si	full	full		2	2							$^3P_0$
15 P				2	3							$^4S_{3/2}$
16 S				2	4							$^3P_2$
17 Cl				2	5							$^2P_{3/2}$
18 Ar				2	6							$^1S_0$
19 K				2	6		1					$^2S_{1/2}$
20 Ca				2	6		2					$^1S_0$
21 Sc				2	6	1	2					$^2D_{3/2}$
22 Ti				2	6	2	2					$^3F_2$
23 V				2	6	3	2					$^4F_{3/2}$
24 Cr				2	6	5	1					$^7S_3$
25 Mn				2	6	5	2					$^6S_{5/2}$
26 Fe				2	6	6	2					$^5D_4$
27 Co	full	ful!		2	6	7	2					$^4F_{9/2}$
28 Ni				2	6	8	2					$^3F_4$
29 Cu				2	6	10	1					$^2S_{1/2}$
30 Zn				2	6	10	2					$^1S_0$
31 Ga				2	6	10	2	1				$^2P_{1/2}$
32 Ge				2	6	10	2	2				$^3P_0$
33 As				2	6	10	2	3				$^4S_{3/2}$
34 Se				2	6	10	2	4				$^3P_2$
35 Br				2	6	10	2	5				$^2P_{3/2}$
36 Kr				2	6	10	2	6				$^1S_0$

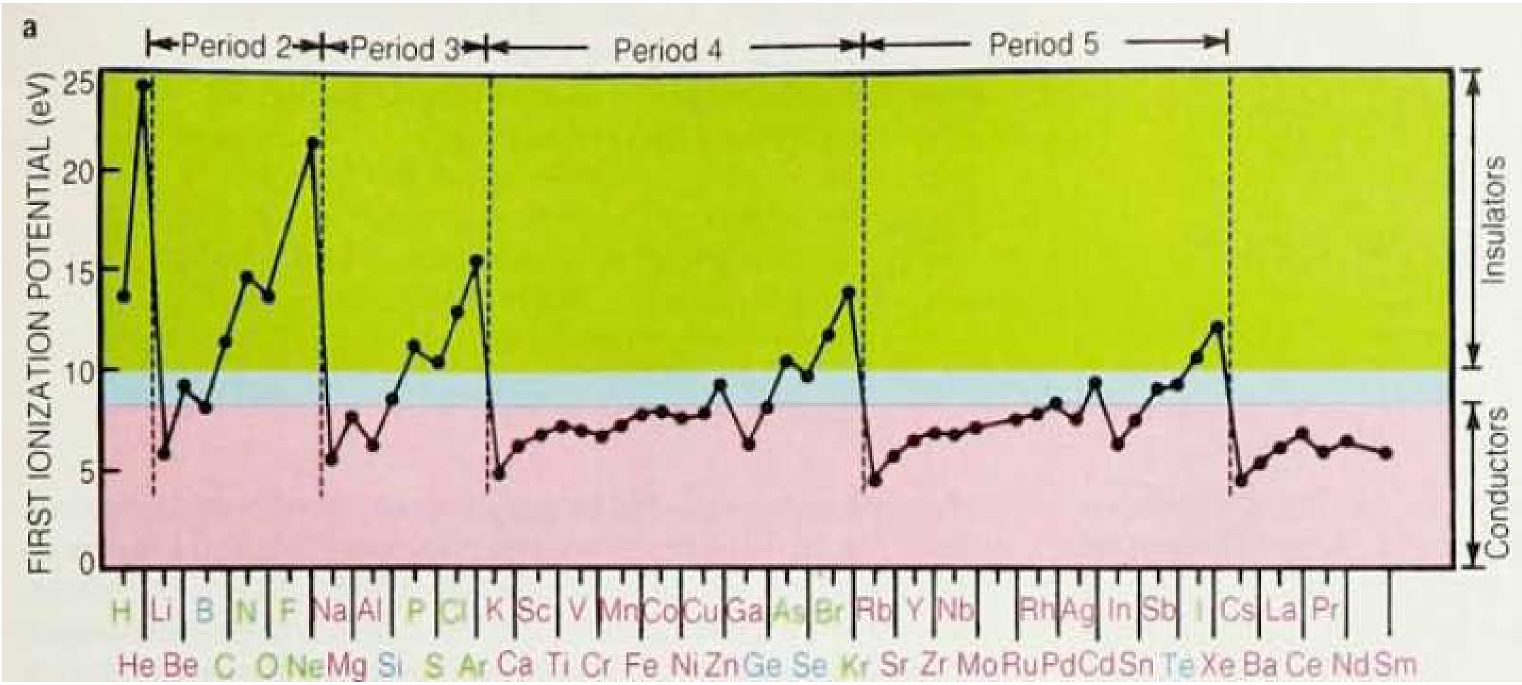
Z \ nl	1s	2s, p	3s, p, d	4s	4p	4d	4f	5s	5p	5d	5f	5g	Ground level
37 Rb				2	6			1					$^2S_{1/2}$
38 Sr				2	6			2					$^1S_0$
39 Y				2	6	1		2					$^2D_{3/2}$
40 Zr				2	6	2		2					$^3F_2$
41 Nb				2	6	4		1					$^6D_{1/2}$
42 Mo				2	6	5		1					$^7S_3$
43 Tc				2	6	5		2					$^6S_{5/2}$
44 Ru				2	6	7		1					$^5F_5$
45 Rh	full	full	full	2	6	8		1					$^4F_{9/2}$
46 Pd				2	6	10							$^1S_0$
47 Ag				2	6	10		1					$^2S_{1/2}$
48 Cd				2	6	10		2					$^1S_0$
49 In				2	6	10		2	1				$^2P_{1/2}$
50 Sn				2	6	10		2	2				$^3P_0$
51 Sb				2	6	10		2	3				$^4S_{3/2}$
52 Te				2	6	10		2	4				$^3P_2$
53 I				2	6	10		2	5				$^2P_{3/2}$
54 Xe				2	6	10		2	6				$^1S_0$

Z	1s	2s, p	3s, p, d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	Ground level
55 Cs				2	6	10		2	6				1	$^2S_{1/2}$
56 Ba				2	6	10		2	6				2	$^1S_0$
57 La				2	6	10		2	6	1			2	$^2D_{3/2}$
58 Ce				2	6	10 mixed configurations								$J = 4$
59 Pr				2	6	10	3	2	6				2	$^4I_{9/2}$
60 Nd				2	6	10	4	2	6				2	$^5I_4$
61 Pm				2	6	10	5	2	6				2	$^6H_{5/2}$
62 Sm				2	6	10	6	2	6				2	$^7F_0$
63 Eu				2	6	10	7	2	6				2	$^8S_{7/2}$
64 Gd				2	6	10	7	2	6	1			2	$^9D_2$
65 Tb				2	6	10	8	2	6	1			2	$^8G_{13/2}$
66 Dy				2	6	10	10	2	6				2	$^5I_8$
67 Ho				2	6	10	11	2	6				2	$^4I_{15/2}$
68 Er				2	6	10	12	2	6				2	$^3H_6$
69 Tm				2	6	10	13	2	6				2	$^2F_{7/2}$
70 Yb	full	full	full	2	6	10	14	2	6				2	$^1S_0$
71 Lu								2	6	1			2	$^2D_{3/2}$
72 Hf								2	6	2			2	$^3F_2$
73 Ta								2	6	3			2	$^4F_{3/2}$
74 W								2	6	4			2	$^5D_0$
75 Re								2	6	5			2	$^6S_{5/2}$
76 Os								2	6	6			2	$^5D_4$
77 Ir								2	6	7			2	$^4F_{9/2}$
78 Pt				full				2	6	9			1	$^3D_3$
79 Au								2	6	10			1	$^2S_{1/2}$
80 Hg								2	6	10			2	$^1S_0$

Z	1s	2s, p	3s, p, d	4s, p, d, f	5s	5p	5d	5f	5g	6s	6p	6d	7s	Ground level
81 Tl					2	6	10			2	1			$^2P_{1/2}$
82 Pb					2	6	10			2	2			$^3P_0$
83 Bi	full	full	full	full	2	6	10			2	3			$^4S_{3/2}$
84 Po					2	6	10			2	4			$^3P_2$
85 At					2	6	10			2	5			$^2P_{3/2}$
86 Rn					2	6	10			2	6			$^1S_0$
87 Fr					2	6	10			2	6		1	$^2S_{1/2}$
88 Ra					2	6	10			2	6		2	$^1S_0$
89 Ac					2	6	10			2	6	1	2	$^2D_{3/2}$
90 Th					2	6	10			2	6	2	2	$^3F_2$
91 Pa					2	6	10	2		2	6	1	2	$^4K_{11/2}$
92 U					2	6	10	3		2	6	1	2	$^5L_6$
93 Np					2	6	10	4		2	6	1	2	$^6L_{11/2}$
94 Pu					2	6	10	6		2	6		2	$^7F_0$
95 Am	full	full	full	full	2	6	10	7		2	6		2	$^8S_{7/2}$
96 Cm					2	6	10	7		2	6	1	2	$^9D_2$
97 Bk					2	6	10	8?		2	6	1?	2	$^8G_{15/2}$?
98 Cf					2	6	10	10?		2	6		2	$^5I_8$?
99 E					2	6	10	11		2	6		2	$^4I_{15/2}$
100 Fm					2	6	10	12		2	6		2	$^3H_6$
101 Mv					2	6	10	13		2	6		2	$^2F_{7/2}$
102 No					2	6	10	14		2	6		2	$^1S_0$
103 Lw					2	6	10	14		2	6	1	2	$^2D_{3/2}$

Evidències espectroscòpiques

Potencials de ionització



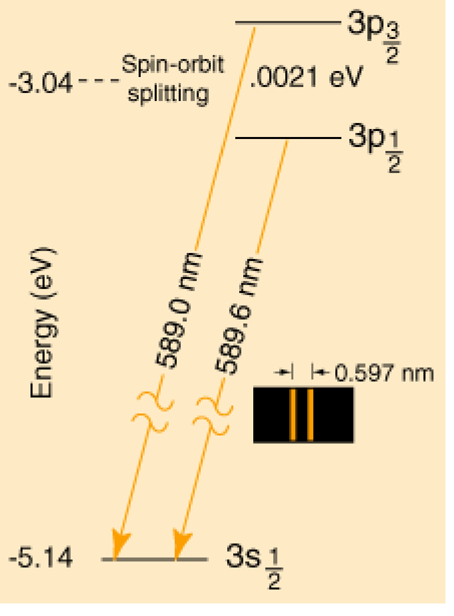
- ❑ ‘Periodicitat’ en *Z*
- ❑ Capa de valència

Espectres òptics

Electrons de valència
Energies eV
Infraroig, visible, UV

Diagrama de termes del Na
de Grotrian

El doblet D del Na



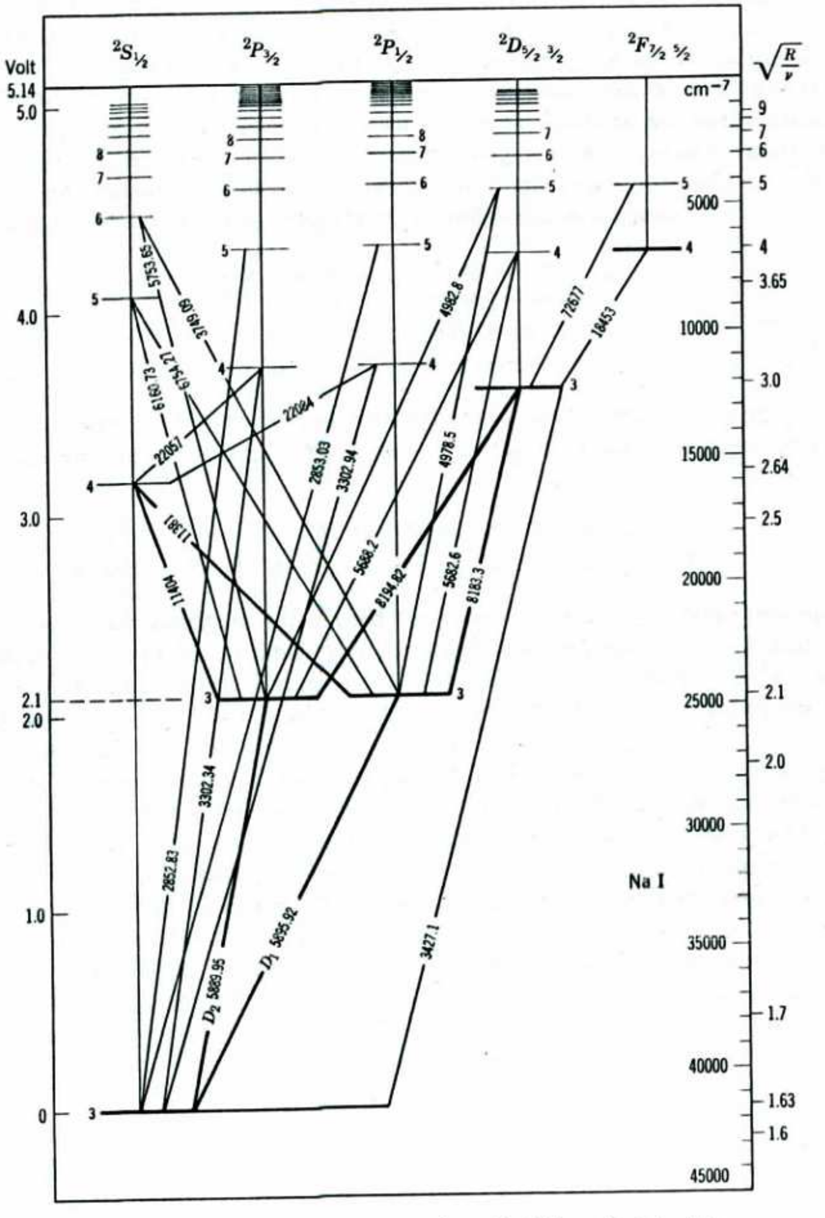


Fig. 1.9 Grotrian diagram for sodium, Na I (from Grotrian [1]).

Espectres de rajos X

Transicions a capes profundes
Energies creixents amb Z
keV

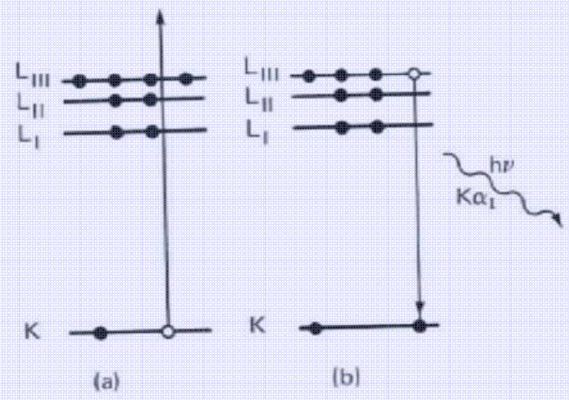


FIG. 23.7 X-ray absorption and fluorescence. (a) Excitation; (b) deexcitation by fluorescence.

Un process alternatiu es l'emissió d'electrons (Auger)

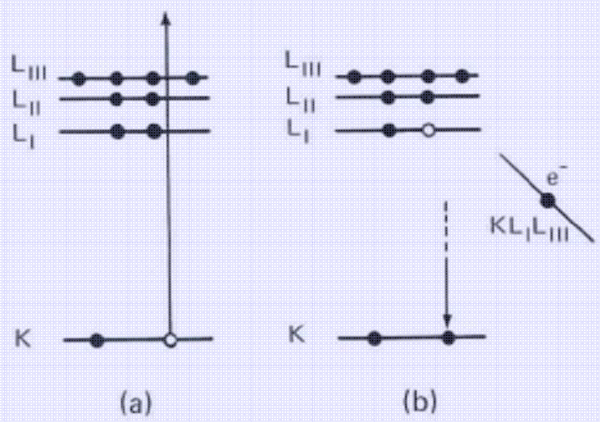


FIG. 23.10 Auger effect. (a) Excitation; (b) by Auger effect.

Transicions a capes profundes

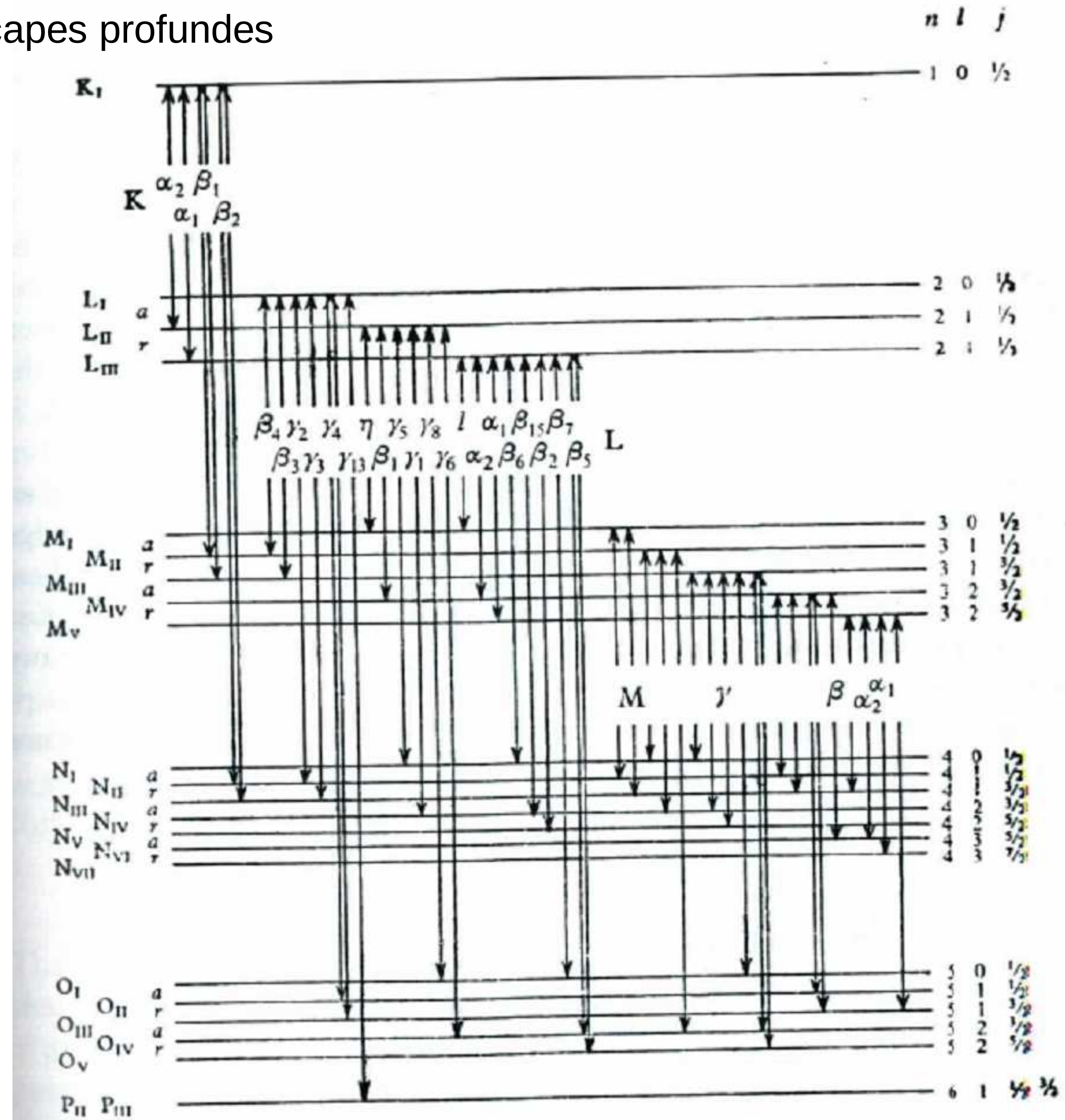


FIG. 23.8 X-ray terms and lines (Kuhn, 1962).

Espectres d'absorbiment de rajos X

Discontinuitats

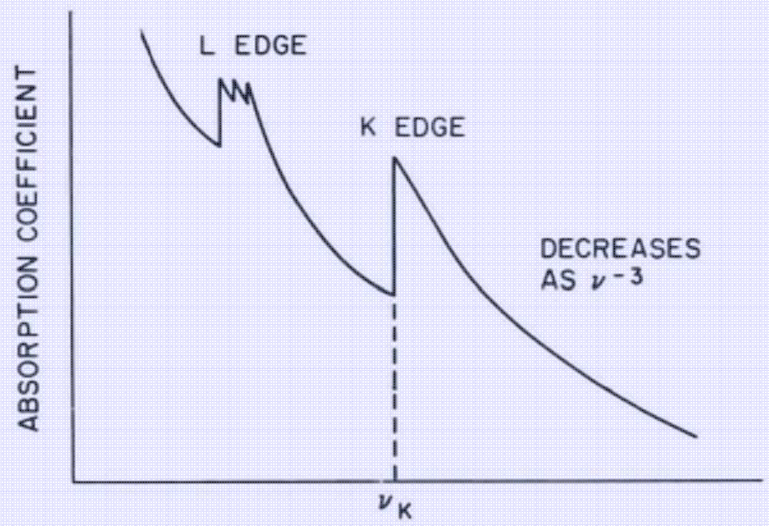


FIG. 23.9 X-ray absorption spectrum.

Energies de rajos X creixents amb *Z*

llei de Moseley

$$\varepsilon_{n\ell} \approx -\frac{(Z-\sigma_{n\ell})^2}{n^2}$$

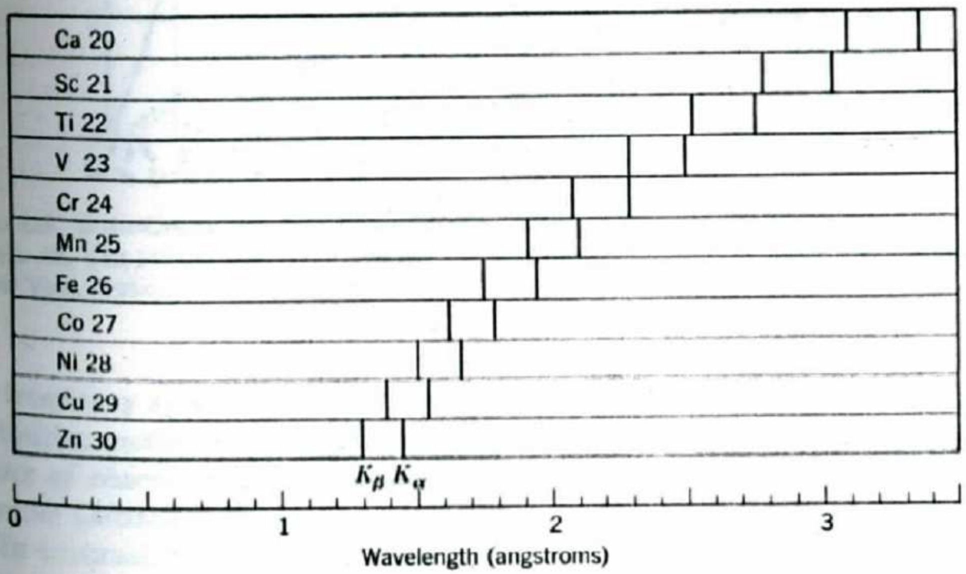
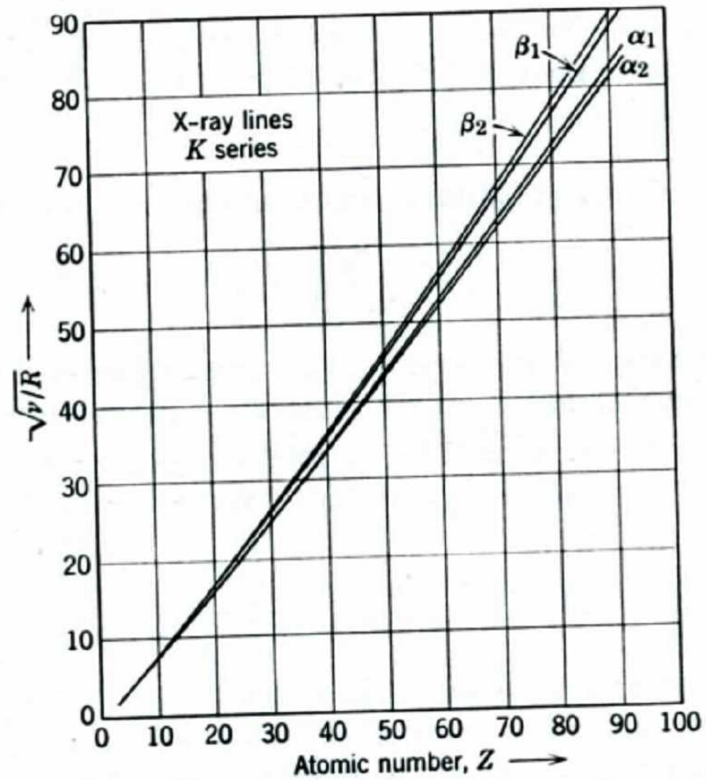


Fig. 1.4 Variation of characteristic x-ray wavelength with atomic number, as observed by Moseley [*Phil. Mag.* **26**, 1024 (1913); redrawn here after H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill, New York (1934)].



(a)

Diagrama de Bohr-Coster

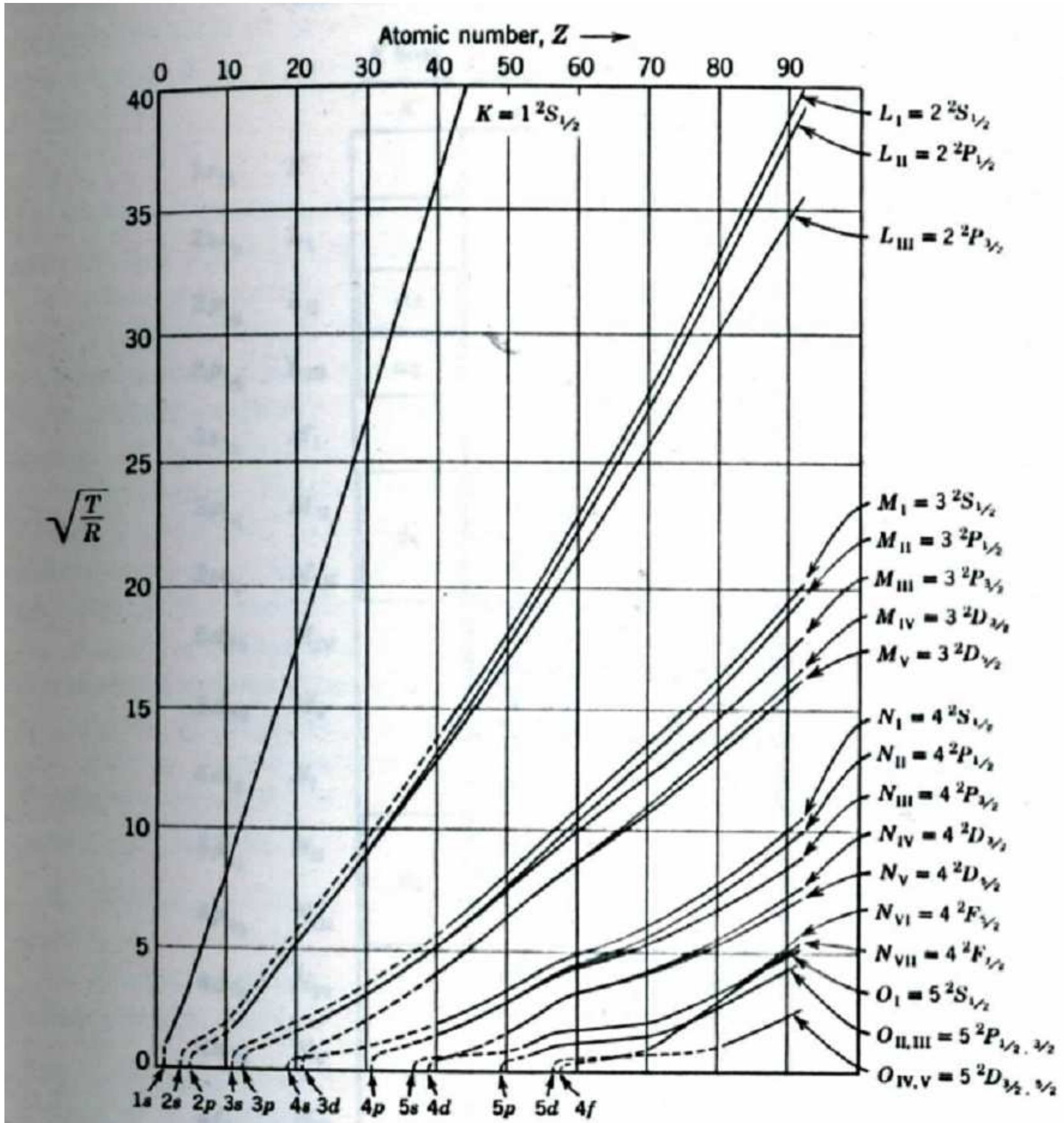


Fig. 1.6 Bohr-Coster diagram of x-ray term values. [After N. Bohr and D. Coster, *Z. Phys.* **12**, 342 (1923), and H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill, New York (1934).]

Representació de de Vault