EM2011, GRUPO D

Conceptos atómicos

Sirven como introducción los apuntes de FC2 de Joaquín Retamosa

Se puede ampliar con el Brasden and Joachaim 'Physics of Atoms and Molecules', libro fácil de conseguir en la biblioteca, en Amazon y en otros recursos

Estudiar sobre todo las trasparencias marcadas en rojo arriba a la izquierda.

El resto también, aunque son más bien complementarias

Espectros atómicos

Para ver qué líneas se verían en los espectros, hay que considerar las reglas de selección. Como pasaba en las desintegraciones β y α, en una transición atómica (o transiciones γ en el núcleo), hay una partícula más en el estado final, en este caso un fotón. La parte radia de la fdo de ese fotón será e^{ikr}

Ahora, k es del orden de las transiciones atómicas, algunos eV. Y r es del orden de las dimensiones atómicas, o sea, digamos 10 Amgstrons o 1 nm.

$1=\hbar c=197.3$ MeV . fm = 1973 eV.Å; si k=10 eV y r=10 Å, kr = 100/1973 < 0.05

Como en el caso de desintegraciones β, el orden más bajo de la expansión de La fdo del fotón (es decir el 1 en $e^{ikr} = 1 + i\, k.r + \ldots$) determina las transiciones dominantes. Esta aproximación se denomina '*aproximación dipolar eléctrica*'.

En esta aproximación las reglas de selección relevantes son: $\Delta l=+1$ ó -1.
$\Delta n=$ cualquiera

Otras líneas no dadas por la transición dipolar eléctrica existen (es el equivalente de las transiciones prohibidas en β) pero son muchísimo menos intensas.

Más sobre unidades

$1\ \text{Å} = 10^{-10}\text{m}$

Constante de Boltzman $k_B = 8{,}6 \times 10^{-6}$ eV /K (ó eV/°C)
A temperatura ambiente (300 K), $k_B\,T = 0{,}027$ eV

En nuestras unidades, $1 = \hbar c = 197.3$ MeV.fm = 1973 eV.Å, se puede dar energía en cm^{-1} o en fm^{-1}.

Sin embargo, en atómica, al contrario que en nuclear, no se toma $\hbar = 1$ sino más bien $h = 1$. Esto hace que tengamos que cambiar nuestras conversiones un poco:

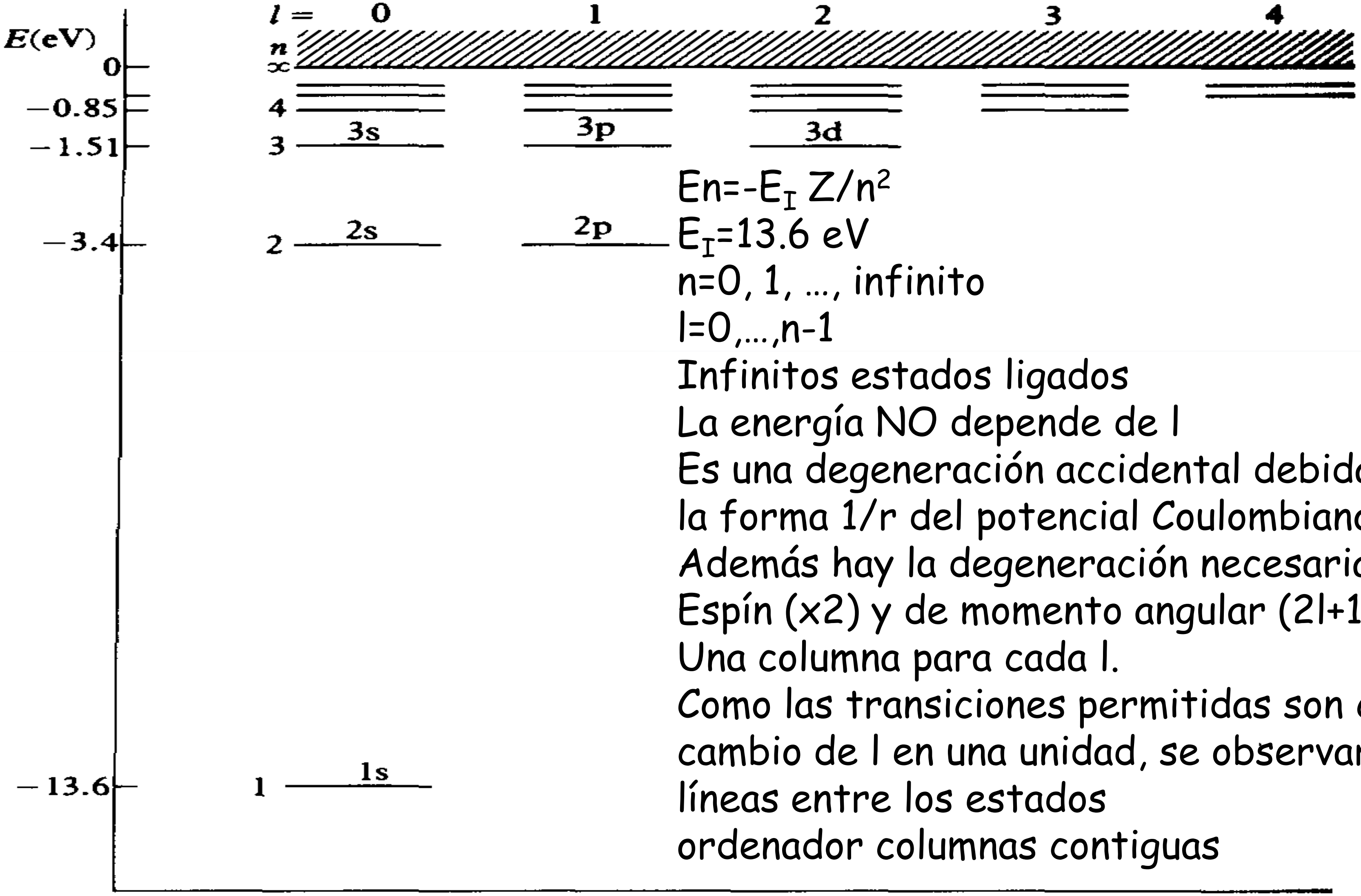
Si $h = 1$, entonces $\hbar = 1./2\pi$

Por tanto:

$1 = hc = \hbar\, c\, 2\,\pi = 1973\ \text{eV. Å}\ 2\,\pi$

Y en conclusion 1 eV=8065 cm^{-1}

Espectro del átomo de H



$En=-E_I\ Z/n^2$

$E_I=13.6$ eV

n=0, 1, …, infinito

l=0,…,n-1

Infinitos estados ligados

La energía NO depende de l

Es una degeneración accidental debida a la forma 1/r del potencial Coulombiano

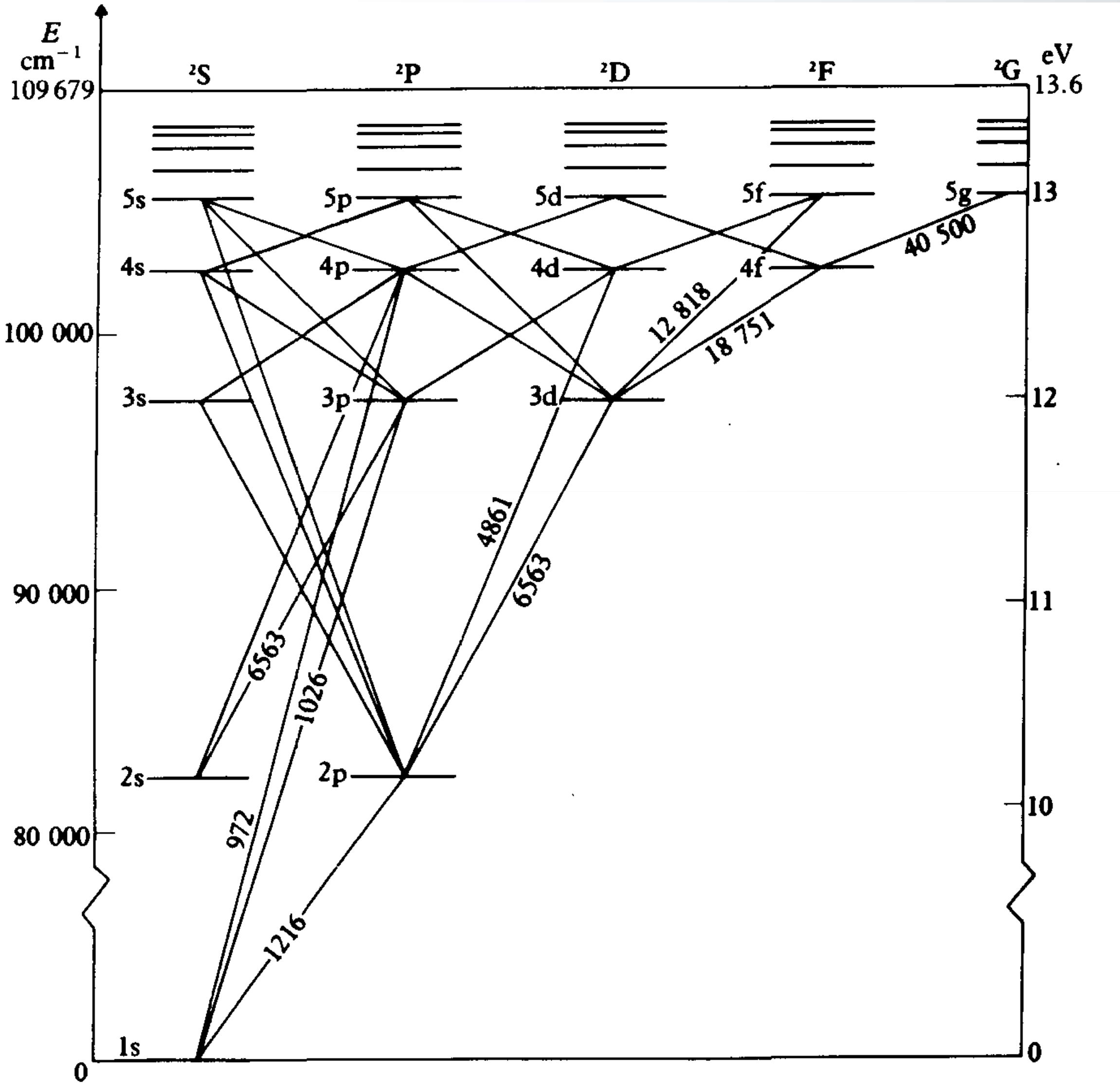
Además hay la degeneración necesaria de Espín (x2) y de momento angular (2l+1)

Una columna para cada l.

Como las transiciones permitidas son con cambio de l en una unidad, se observarán líneas entre los estados ordenador columnas contiguas

3.2 Energy-level diagram for atomic hydrogen.

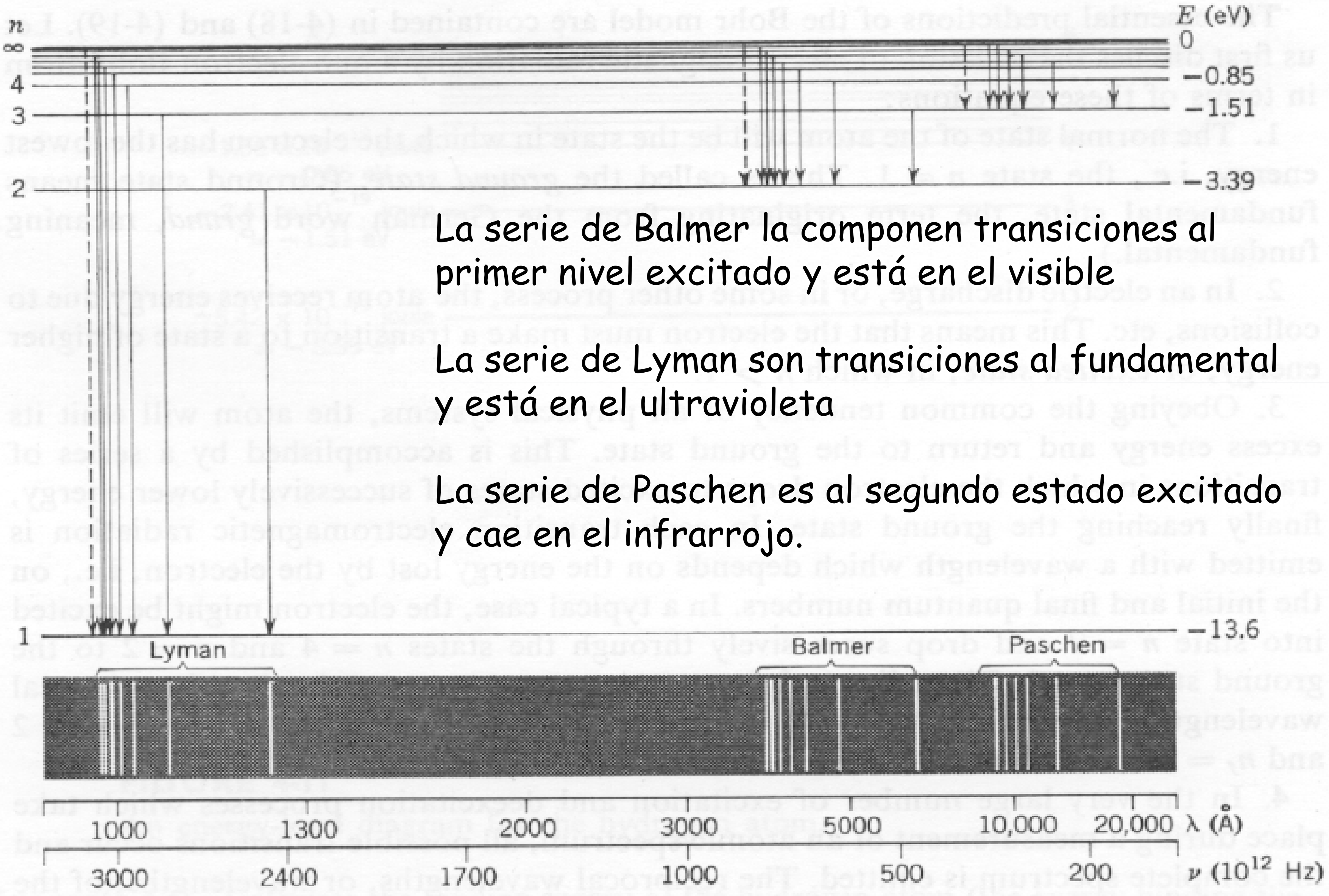
Espectro del átomo de H



Así, las líneas del espectro se determinan con ayuda del diagrama de Grotrian.

Como las transiciones permitidas son con cambio de l en una unidad, se observarán líneas entre los estados en columnas contiguas

Espectro del átomo de H

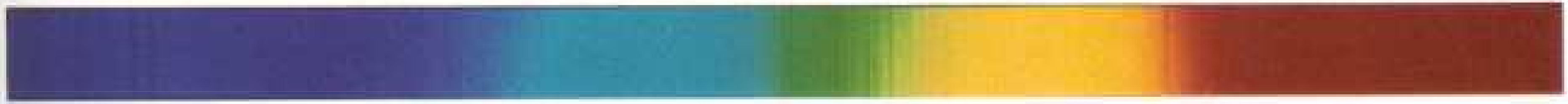


La serie de Balmer la componen transiciones al primer nivel excitado y está en el visible

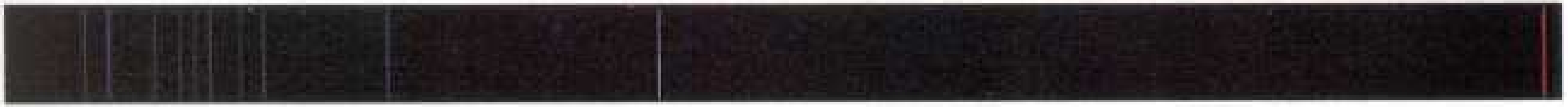
La serie de Lyman son transiciones al fundamental y está en el ultravioleta

La serie de Paschen es al segundo estado excitado y cae en el infrarrojo.

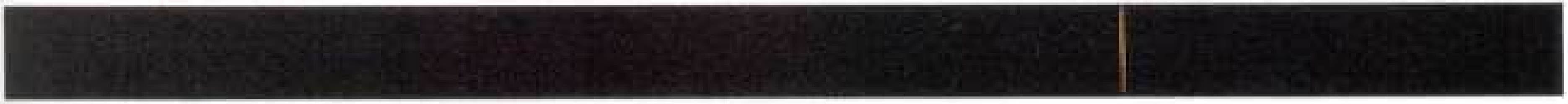
Espectro del átomo de H



Solar absorption spectrum (Fraunhofer lines)



Atomic hydrogen (H)



Sodium (Na)

Algunas funciones radiales hidrogenoides

$$R_{10}(r) = 2(Z/a_0)^{3/2}\exp(-Zr/a_0)$$

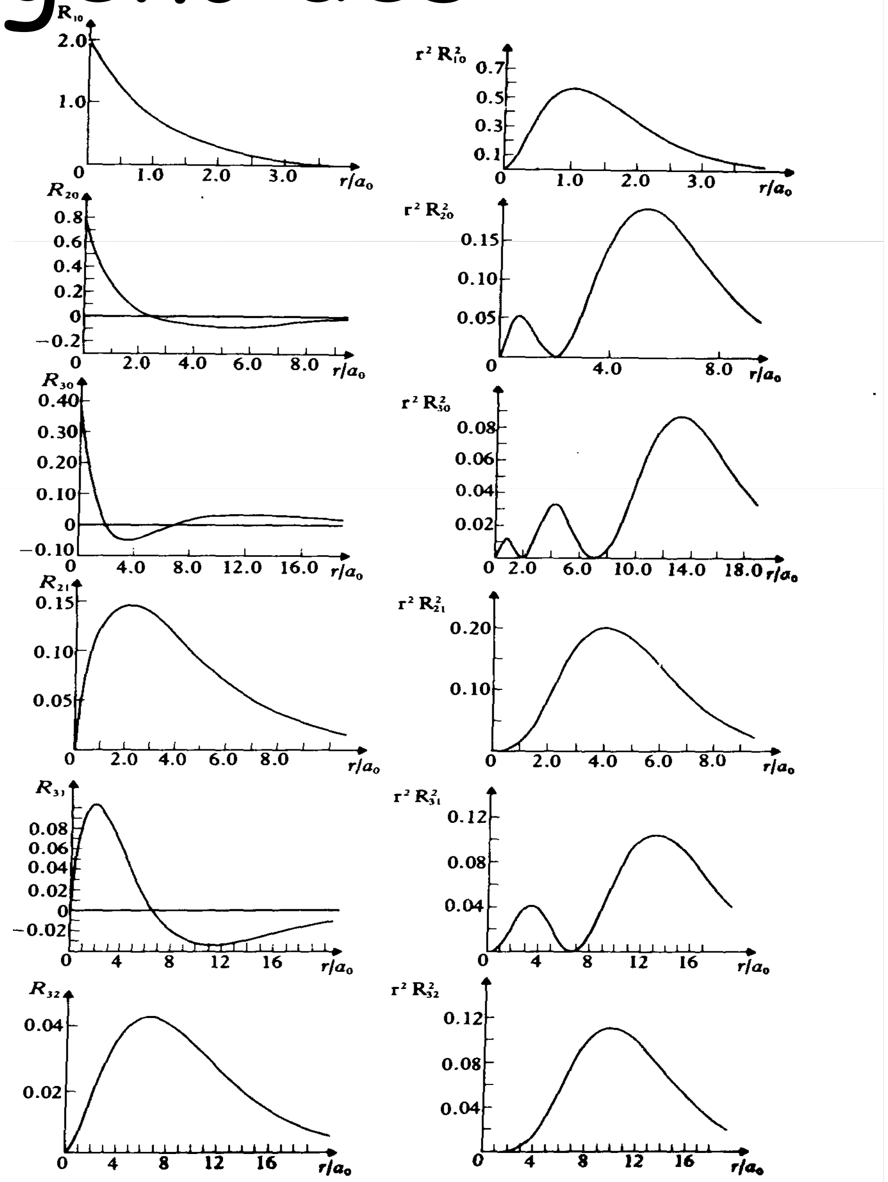
$$R_{20}(r) = 2(Z/2a_0)^{3/2}(1 - Zr/2a_0)\exp(-Zr/2a_0)$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}(Z/2a_0)^{3/2}(Zr/a_0)\exp(-Zr/2a_0)$$

$$R_{30}(r) = 2(Z/3a_0)^{3/2}(1 - 2Zr/3a_0 + 2Z^2r^2/27a_0^2)\exp(-Zr/3a_0)$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9}(Z/3a_0)^{3/2}(1 - Zr/6a_0)(Zr/a_0)\exp(-Zr/3a_0)$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}}(Z/3a_0)^{3/2}(Zr/a_0)^2\exp(-Zr/3a_0)$$



3.3 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen.

Using the normalised radial eigenfunctions [3.53] it is found that

$$\langle r \rangle_{nlm} = a_\mu \frac{n^2}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right\} \qquad [3.68]$$

which is seen to agree with [3.66] when $n = 1$ and $l = 0$. We remark from [3.68] that $\langle r \rangle_{nlm}$, which we may interpret as the 'size' of the atom, is inversely proportional to Z and roughly proportional to n^2, in agreement with the discussion following [3.63]. In fact, we see that for s-states ($l = 0$) $\langle r \rangle_{nlm}$ is directly proportional to n^2; for states with $l \neq 0$ the deviations from this proportionality are small.

Rydberg atoms

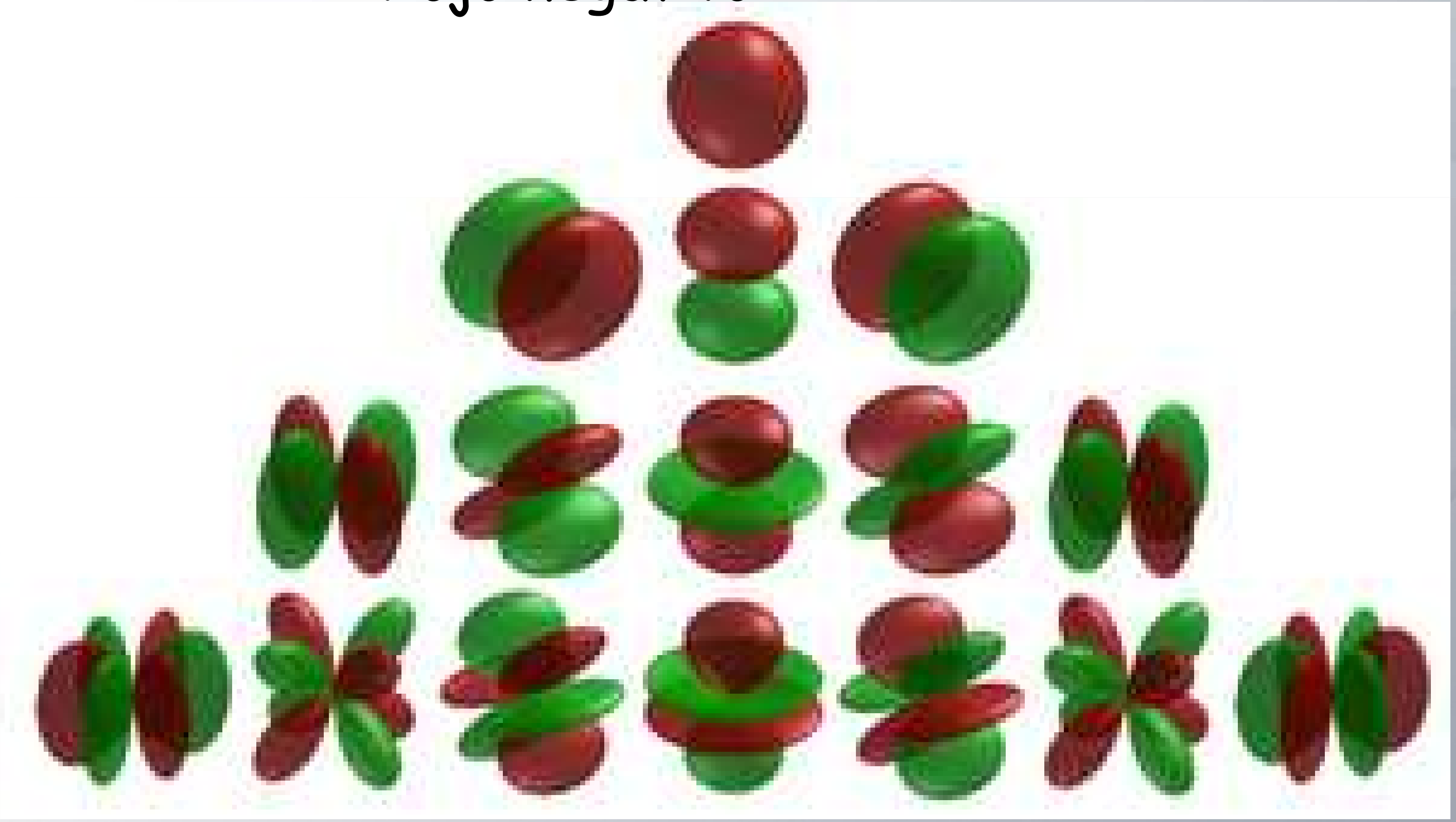
A highly excited atom (or ion) has an electron with a large principal quantum number n. The electron (or the atom) is said to be in a 'high Rydberg state' and the highly excited atom is also referred to more simply as a 'Rydberg atom'.

Table 3.3 Comparison of some characteristic quantities of the hydrogen atom for different values of the principal quantum number n

Quantity	$n = 1$	*Arbitrary* n	$n = 100$
Radius a_n of Bohr orbit (in m)	$a_0 \simeq 5.3 \times 10^{-11}$	$\simeq n^2 a_0$	5.3×10^{-7}
Geometric cross-section πa_n^2 (in m^2)	$\pi a_0^2 \simeq 8.8 \times 10^{-21}$	$\simeq n^4 \pi a_0^2$	8.8×10^{-13}
Binding energy E_n (in eV)	$I_P^H \simeq 13.6$	I_P^H / n^2	1.36×10^{-3}
Energy separation ΔE between adjacent levels (in eV)		$\simeq 2 I_P^H / n^3$ (n large)	2.7×10^{-5}
Root-mean-square velocity of electron v_n (in ms^{-1})	$v_0 \sim c\alpha$ $\simeq 2.2 \times 10^6$	$\simeq v_0 / n$	2.2×10^4
Period T_n (in s)	$T_0 = 1.5 \times 10^{-16}$	$\simeq n^3 T_0$	1.5×10^{-10}

Algunas partes angulares (armónicos esféricos)

Verde: positivo
Rojo:negativo



L=0

L=1

L=2

L=3

Algunas partes angulares (armónicos esféricos)

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{-i\varphi}$$

$$Y_1^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\cos\theta$$

$$Y_1^1(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{i\varphi}$$

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin^2\theta\, e^{-2i\varphi}$$

$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\sin\theta\,\cos\theta\, e^{-i\varphi}$$

$$Y_2^0(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(3\cos^2\theta - 1)$$

$$Y_2^1(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{15}{2\pi}}\,\sin\theta\,\cos\theta\, e^{i\varphi}$$

$$Y_2^2(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin^2\theta\, e^{2i\varphi}$$

X

Átomos multi-electrónicos

Se utiliza la aproximación de campo medio y se etiquetan y ordenan los niveles por el n y l de cada nivel. El valor de n define una CAPA y, para un n dado, cada l define una subcapa.

Una subcapa llena tiene simetría esférica y L=0, S=0, J=0. Los electrones en las capas (y subcapas) llenas no participan en el enlace químico ni en los espectros

Las propiedades químicas (electrones de valencia) y del espectro de los átomos (electrones ópticos) multi-electrónicos vienen definidas por los electrones externos, es decir, de las últimas subcapas incompletas.

Notación espectroscópica. Cada 'término' se denota por:

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

Átomos multi-electrónicos

Para muchos electrones, los más externos están 'apantallados' por los electrones internos. Por tanto, lq carga nuclear que ven es menor que Z. La forma del potencial ya no es Z/r, por tanto se rompe la degeneración accidental.

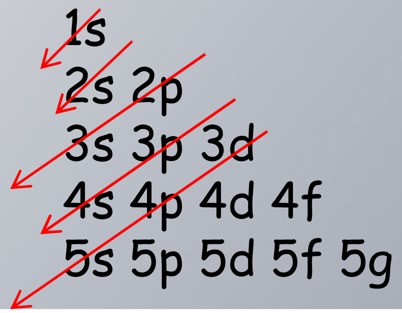
Las fdo que están más lejos del núcleo están más apantalladas, los electrones ven menos carga positiva, tienen menos energía de ligadura.

Así que, dentro de cada n, a menor l, más energía de ligadura.

La energía de ligadura también decrece con n.

En un cierto punto, para n's altos (4 y siguientes) tiene más energía de ligadura el n mayor, con tal de mantener un l bajo.

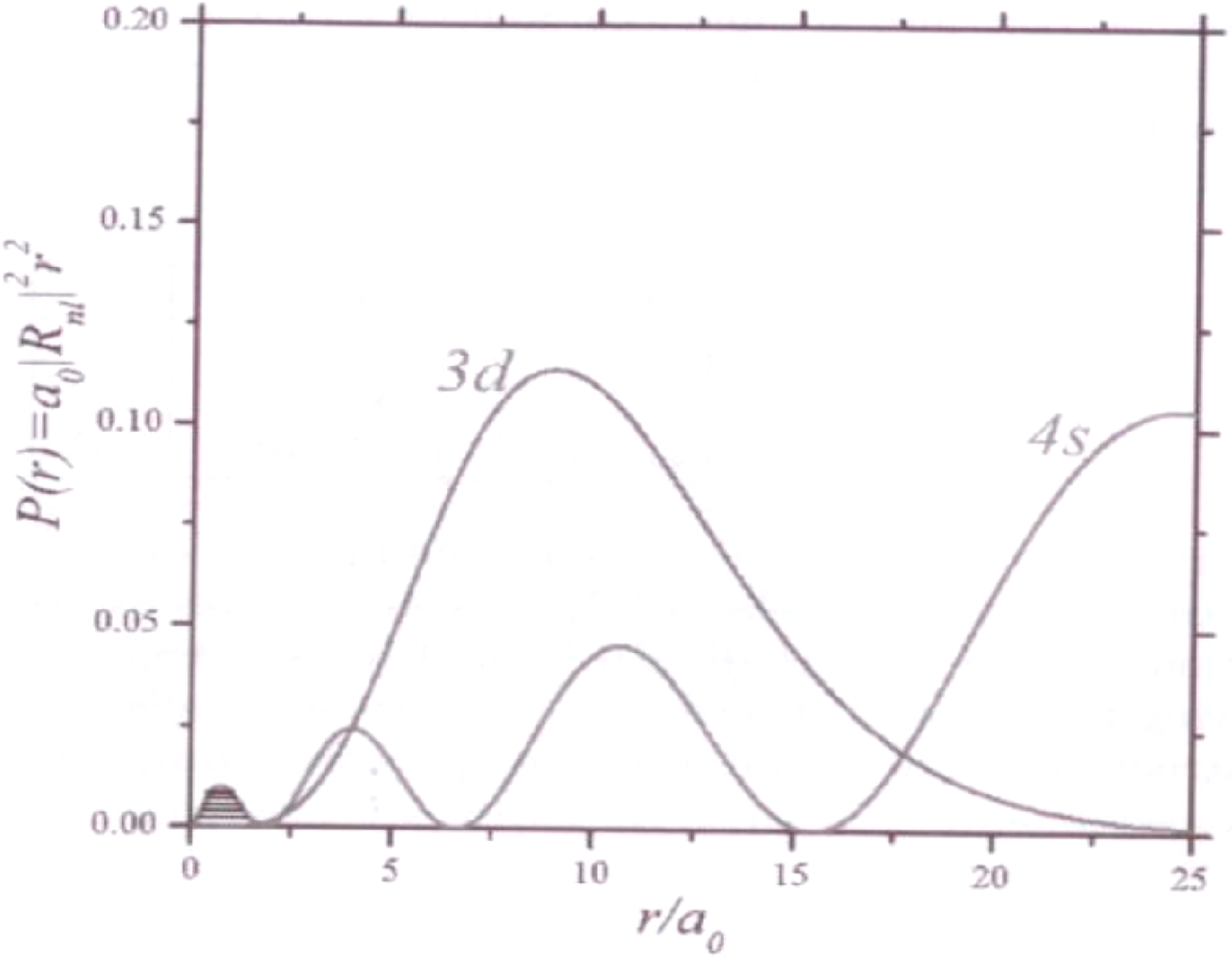
Hay una regla nemotécnica para recordar el orden de llenado:



1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f 5g

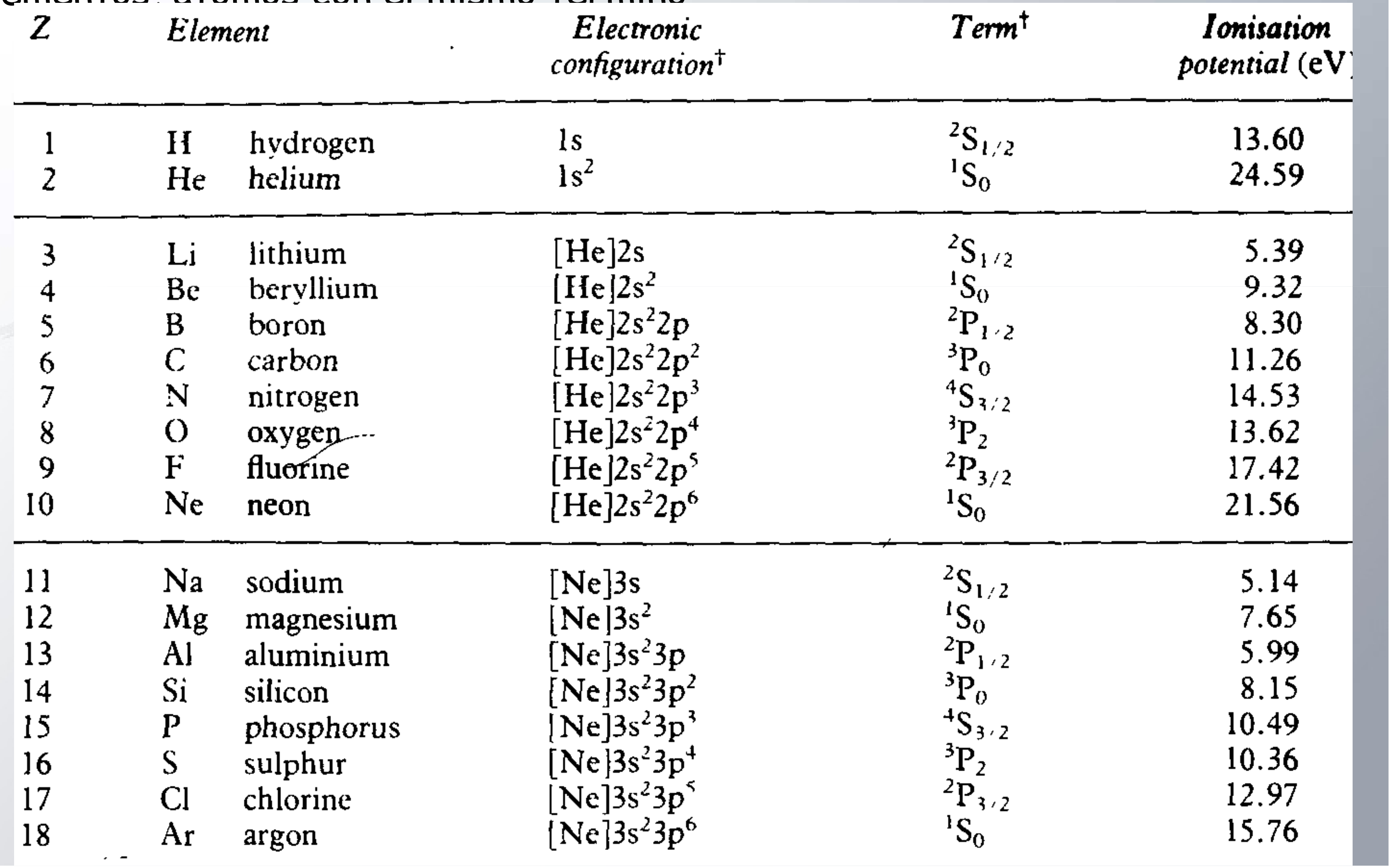
X

Los electrones de la capa 4s están más lejos del núcleo que los de la 3d

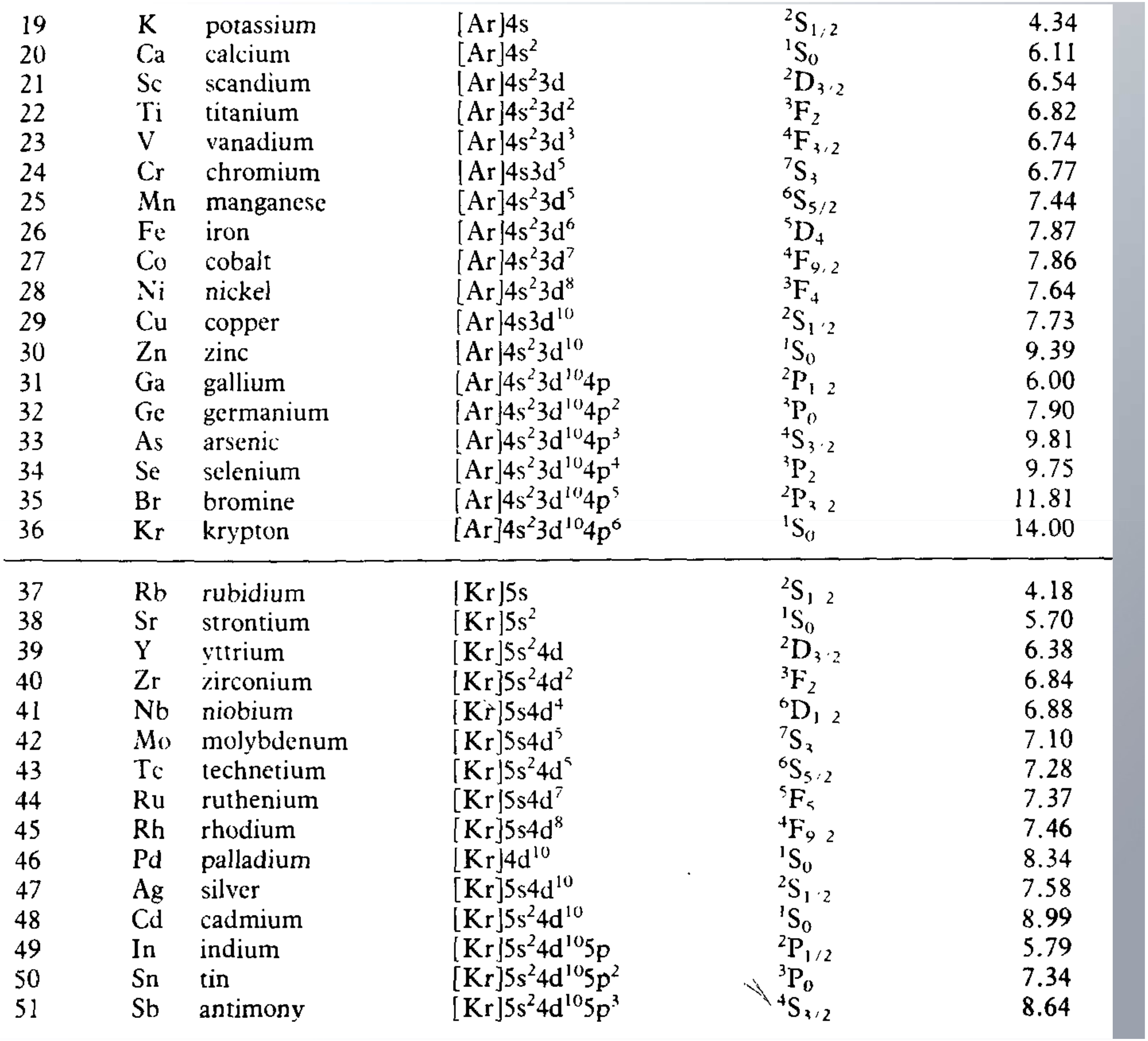


Átomos multi-electrónicos

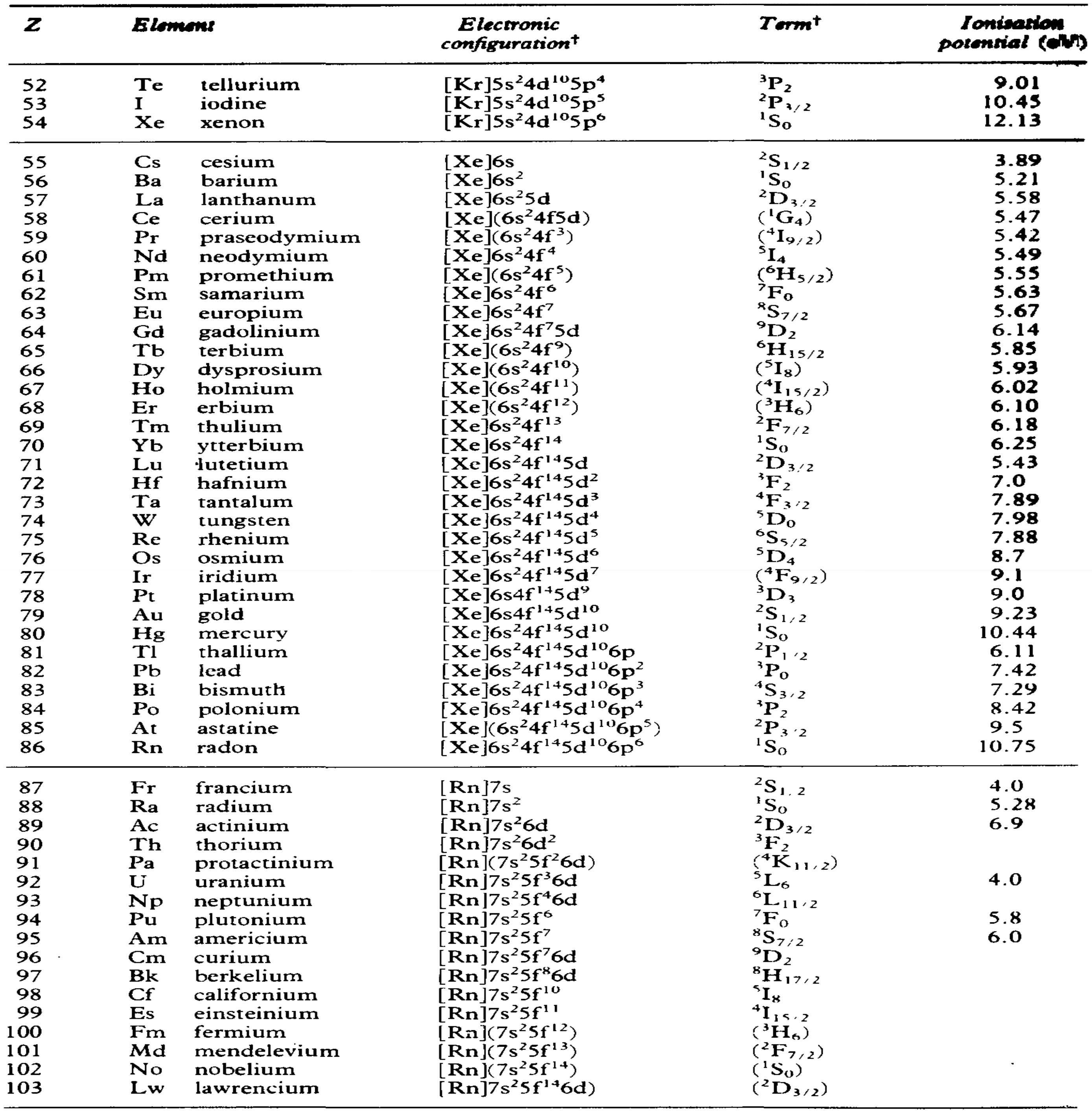
La repetición de las mismas subcapas externas (solo cambia n) sin llenar da lugar a comportamientos químicos similares: La tabla periódica de los elementos, átomos con el mismo término



Z	*Element*		*Electronic configuration*†	*Term*†	*Ionisation potential* (eV
1	H	hydrogen	$1s$	$^2S_{1/2}$	13.60
2	He	helium	$1s^2$	$^1S_0$	24.59
3	Li	lithium	[He]$2s$	$^2S_{1/2}$	5.39
4	Be	beryllium	[He]$2s^2$	$^1S_0$	9.32
5	B	boron	[He]$2s^2 2p$	$^2P_{1/2}$	8.30
6	C	carbon	[He]$2s^2 2p^2$	$^3P_0$	11.26
7	N	nitrogen	[He]$2s^2 2p^3$	$^4S_{3/2}$	14.53
8	O	oxygen	[He]$2s^2 2p^4$	$^3P_2$	13.62
9	F	fluorine	[He]$2s^2 2p^5$	$^2P_{3/2}$	17.42
10	Ne	neon	[He]$2s^2 2p^6$	$^1S_0$	21.56
11	Na	sodium	[Ne]$3s$	$^2S_{1/2}$	5.14
12	Mg	magnesium	[Ne]$3s^2$	$^1S_0$	7.65
13	Al	aluminium	[Ne]$3s^2 3p$	$^2P_{1/2}$	5.99
14	Si	silicon	[Ne]$3s^2 3p^2$	$^3P_0$	8.15
15	P	phosphorus	[Ne]$3s^2 3p^3$	$^4S_{3/2}$	10.49
16	S	sulphur	[Ne]$3s^2 3p^4$	$^3P_2$	10.36
17	Cl	chlorine	[Ne]$3s^2 3p^5$	$^2P_{3/2}$	12.97
18	Ar	argon	[Ne]$3s^2 3p^6$	$^1S_0$	15.76



19	K	potassium	[Ar]$4s$	$^2S_{1/2}$	4.34
20	Ca	calcium	[Ar]$4s^2$	$^1S_0$	6.11
21	Sc	scandium	[Ar]$4s^23d$	$^2D_{3/2}$	6.54
22	Ti	titanium	[Ar]$4s^23d^2$	$^3F_2$	6.82
23	V	vanadium	[Ar]$4s^23d^3$	$^4F_{3/2}$	6.74
24	Cr	chromium	[Ar]$4s3d^5$	$^7S_3$	6.77
25	Mn	manganese	[Ar]$4s^23d^5$	$^6S_{5/2}$	7.44
26	Fe	iron	[Ar]$4s^23d^6$	$^5D_4$	7.87
27	Co	cobalt	[Ar]$4s^23d^7$	$^4F_{9/2}$	7.86
28	Ni	nickel	[Ar]$4s^23d^8$	$^3F_4$	7.64
29	Cu	copper	[Ar]$4s3d^{10}$	$^2S_{1/2}$	7.73
30	Zn	zinc	[Ar]$4s^23d^{10}$	$^1S_0$	9.39
31	Ga	gallium	[Ar]$4s^23d^{10}4p$	$^2P_{1/2}$	6.00
32	Ge	germanium	[Ar]$4s^23d^{10}4p^2$	$^3P_0$	7.90
33	As	arsenic	[Ar]$4s^23d^{10}4p^3$	$^4S_{3/2}$	9.81
34	Se	selenium	[Ar]$4s^23d^{10}4p^4$	$^3P_2$	9.75
35	Br	bromine	[Ar]$4s^23d^{10}4p^5$	$^2P_{3/2}$	11.81
36	Kr	krypton	[Ar]$4s^23d^{10}4p^6$	$^1S_0$	14.00
37	Rb	rubidium	[Kr]$5s$	$^2S_{1/2}$	4.18
38	Sr	strontium	[Kr]$5s^2$	$^1S_0$	5.70
39	Y	yttrium	[Kr]$5s^24d$	$^2D_{3/2}$	6.38
40	Zr	zirconium	[Kr]$5s^24d^2$	$^3F_2$	6.84
41	Nb	niobium	[Kr]$5s4d^4$	$^6D_{1/2}$	6.88
42	Mo	molybdenum	[Kr]$5s4d^5$	$^7S_3$	7.10
43	Tc	technetium	[Kr]$5s^24d^5$	$^6S_{5/2}$	7.28
44	Ru	ruthenium	[Kr]$5s4d^7$	$^5F_5$	7.37
45	Rh	rhodium	[Kr]$5s4d^8$	$^4F_{9/2}$	7.46
46	Pd	palladium	[Kr]$4d^{10}$	$^1S_0$	8.34
47	Ag	silver	[Kr]$5s4d^{10}$	$^2S_{1/2}$	7.58
48	Cd	cadmium	[Kr]$5s^24d^{10}$	$^1S_0$	8.99
49	In	indium	[Kr]$5s^24d^{10}5p$	$^2P_{1/2}$	5.79
50	Sn	tin	[Kr]$5s^24d^{10}5p^2$	$^3P_0$	7.34
51	Sb	antimony	[Kr]$5s^24d^{10}5p^3$	$^4S_{3/2}$	8.64



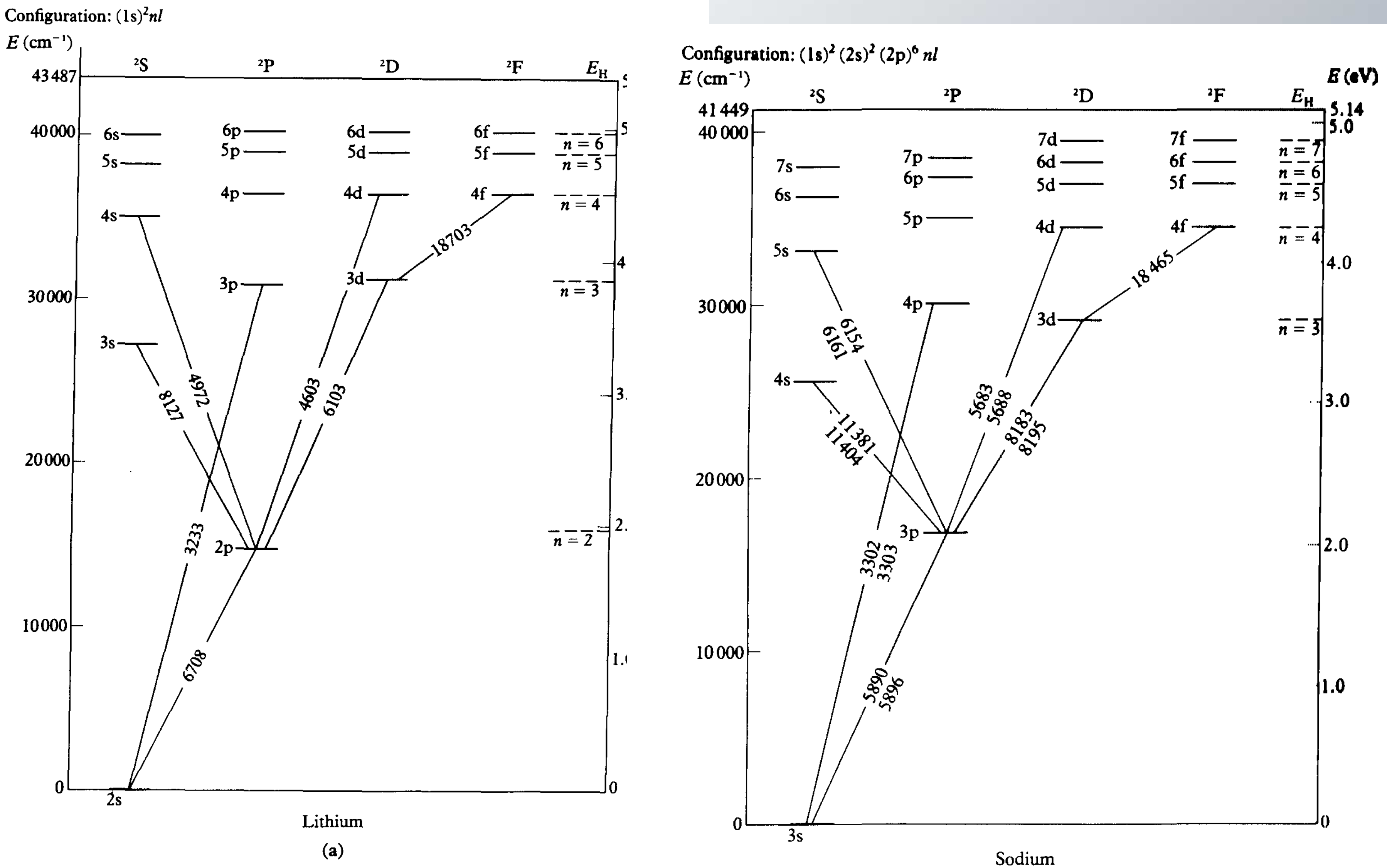
Z	Element		Electronic configuration†	Term†	Ionisation potential (eV)
52	Te	tellurium	$[Kr]5s^24d^{10}5p^4$	$^3P_2$	9.01
53	I	iodine	$[Kr]5s^24d^{10}5p^5$	$^2P_{3/2}$	10.45
54	Xe	xenon	$[Kr]5s^24d^{10}5p^6$	$^1S_0$	12.13
55	Cs	cesium	$[Xe]6s$	$^2S_{1/2}$	3.89
56	Ba	barium	$[Xe]6s^2$	$^1S_0$	5.21
57	La	lanthanum	$[Xe]6s^25d$	$^2D_{3/2}$	5.58
58	Ce	cerium	$[Xe](6s^24f5d)$	$(^1G_4)$	5.47
59	Pr	praseodymium	$[Xe](6s^24f^3)$	$(^4I_{9/2})$	5.42
60	Nd	neodymium	$[Xe]6s^24f^4$	$^5I_4$	5.49
61	Pm	promethium	$[Xe](6s^24f^5)$	$(^6H_{5/2})$	5.55
62	Sm	samarium	$[Xe]6s^24f^6$	$^7F_0$	5.63
63	Eu	europium	$[Xe]6s^24f^7$	$^8S_{7/2}$	5.67
64	Gd	gadolinium	$[Xe]6s^24f^75d$	$^9D_2$	6.14
65	Tb	terbium	$[Xe](6s^24f^9)$	$^6H_{15/2}$	5.85
66	Dy	dysprosium	$[Xe](6s^24f^{10})$	$(^5I_8)$	5.93
67	Ho	holmium	$[Xe](6s^24f^{11})$	$(^4I_{15/2})$	6.02
68	Er	erbium	$[Xe](6s^24f^{12})$	$(^3H_6)$	6.10
69	Tm	thulium	$[Xe]6s^24f^{13}$	$^2F_{7/2}$	6.18
70	Yb	ytterbium	$[Xe]6s^24f^{14}$	$^1S_0$	6.25
71	Lu	lutetium	$[Xe]6s^24f^{14}5d$	$^2D_{3/2}$	5.43
72	Hf	hafnium	$[Xe]6s^24f^{14}5d^2$	$^3F_2$	7.0
73	Ta	tantalum	$[Xe]6s^24f^{14}5d^3$	$^4F_{3/2}$	7.89
74	W	tungsten	$[Xe]6s^24f^{14}5d^4$	$^5D_0$	7.98
75	Re	rhenium	$[Xe]6s^24f^{14}5d^5$	$^6S_{5/2}$	7.88
76	Os	osmium	$[Xe]6s^24f^{14}5d^6$	$^5D_4$	8.7
77	Ir	iridium	$[Xe]6s^24f^{14}5d^7$	$(^4F_{9/2})$	9.1
78	Pt	platinum	$[Xe]6s4f^{14}5d^9$	$^3D_3$	9.0
79	Au	gold	$[Xe]6s4f^{14}5d^{10}$	$^2S_{1/2}$	9.23
80	Hg	mercury	$[Xe]6s^24f^{14}5d^{10}$	$^1S_0$	10.44
81	Tl	thallium	$[Xe]6s^24f^{14}5d^{10}6p$	$^2P_{1/2}$	6.11
82	Pb	lead	$[Xe]6s^24f^{14}5d^{10}6p^2$	$^3P_0$	7.42
83	Bi	bismuth	$[Xe]6s^24f^{14}5d^{10}6p^3$	$^4S_{3/2}$	7.29
84	Po	polonium	$[Xe]6s^24f^{14}5d^{10}6p^4$	$^3P_2$	8.42
85	At	astatine	$[Xe](6s^24f^{14}5d^{10}6p^5)$	$^2P_{3/2}$	9.5
86	Rn	radon	$[Xe]6s^24f^{14}5d^{10}6p^6$	$^1S_0$	10.75
87	Fr	francium	$[Rn]7s$	$^2S_{1/2}$	4.0
88	Ra	radium	$[Rn]7s^2$	$^1S_0$	5.28
89	Ac	actinium	$[Rn]7s^26d$	$^2D_{3/2}$	6.9
90	Th	thorium	$[Rn]7s^26d^2$	$^3F_2$	
91	Pa	protactinium	$[Rn](7s^25f^26d)$	$(^4K_{11/2})$	
92	U	uranium	$[Rn]7s^25f^36d$	$^5L_6$	4.0
93	Np	neptunium	$[Rn]7s^25f^46d$	$^6L_{11/2}$	
94	Pu	plutonium	$[Rn]7s^25f^6$	$^7F_0$	5.8
95	Am	americium	$[Rn]7s^25f^7$	$^8S_{7/2}$	6.0
96	Cm	curium	$[Rn]7s^25f^76d$	$^9D_2$	
97	Bk	berkelium	$[Rn]7s^25f^86d$	$^8H_{17/2}$	
98	Cf	californium	$[Rn]7s^25f^{10}$	$^5I_8$	
99	Es	einsteinium	$[Rn]7s^25f^{11}$	$^4I_{15/2}$	
100	Fm	fermium	$[Rn](7s^25f^{12})$	$(^3H_6)$	
101	Md	mendelevium	$[Rn](7s^25f^{13})$	$(^2F_{7/2})$	
102	No	nobelium	$[Rn](7s^25f^{14})$	$(^1S_0)$	
103	Lw	lawrencium	$[Rn]7s^25f^{14}6d)$	$(^2D_{3/2})$	

† Configurations and terms in parentheses are estimated.

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
1	1 H 1.008																	2 He 4.003
2	3 Li 6.939	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
3	11 Na 22.990	12 Mg 24.312											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
4	19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
6	55 Cs 132.91	56 Ba 137.34	57† La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89‡ Ac 227	104	105													

† Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
† Actinides	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk 249	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lr (257)

Alcalinos: (completo) ns



Lithium

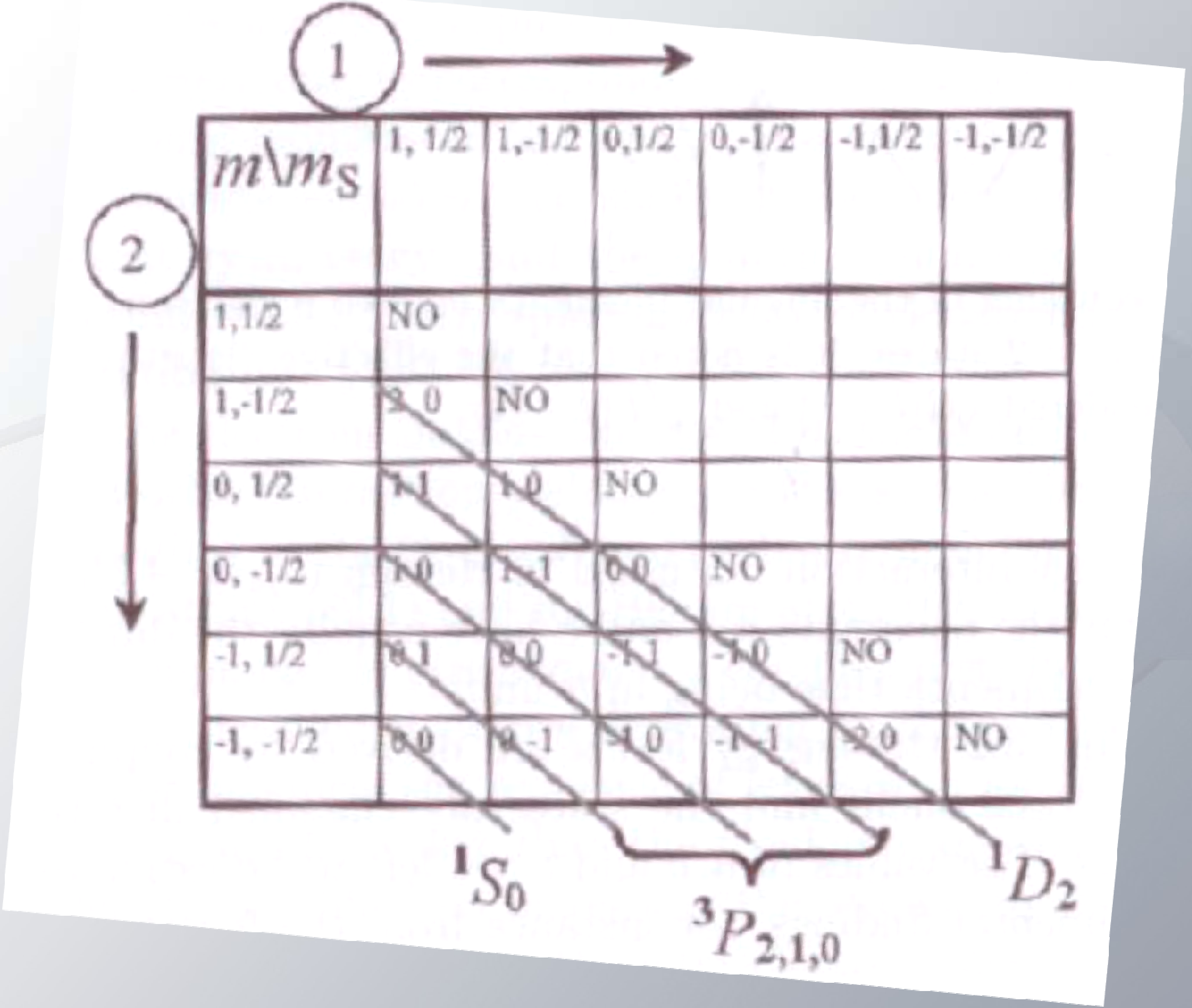
(a)

Sodium

(b)

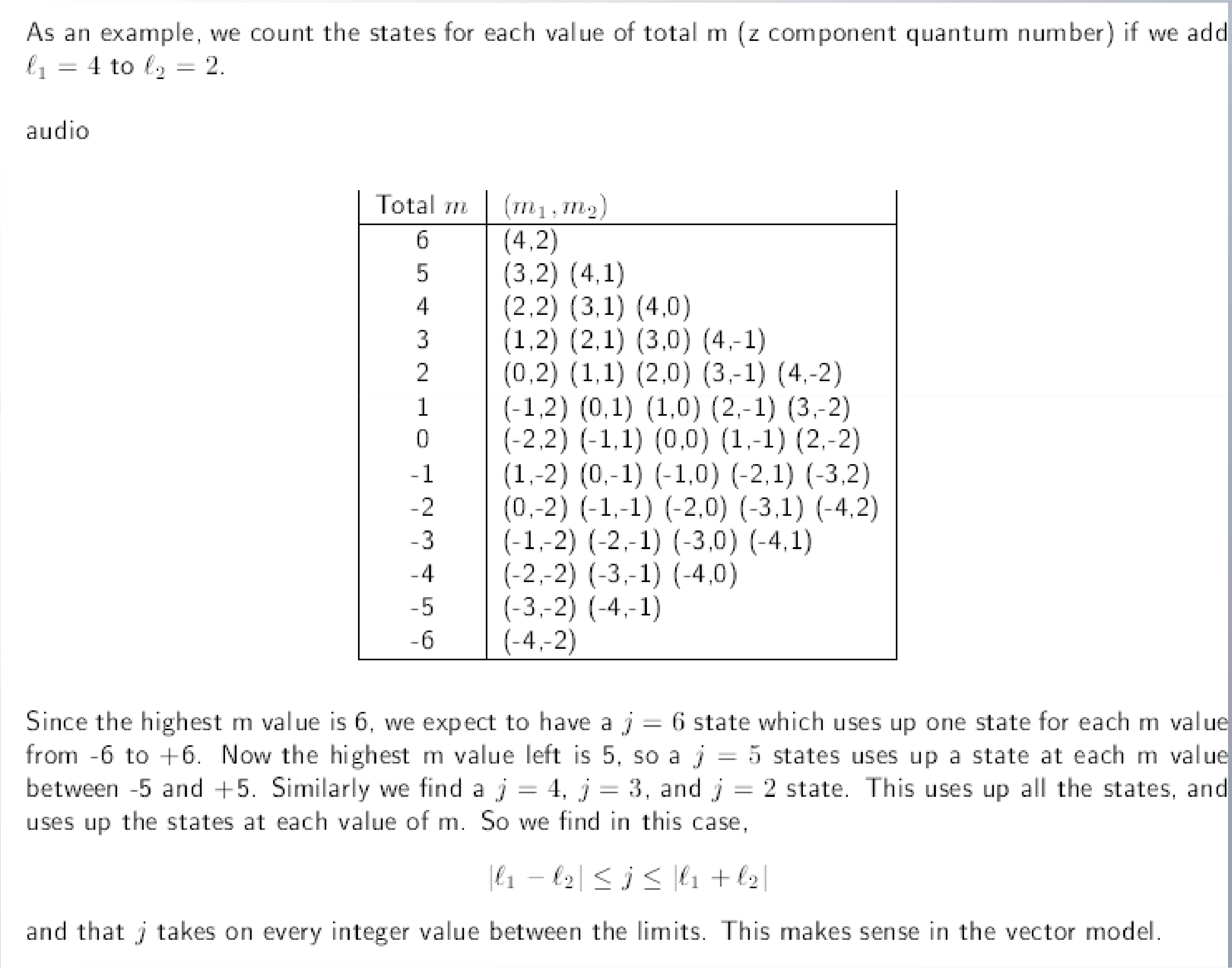
8.1 Grotrian diagrams of energy levels and transitions in (a) lithium and (b) sodium. En
shown relative to the ground state, with the horizontal line at the top of each diagram sh
ionisation potential of the ground state. The column headed E_H shows the corresponding
of the levels of atomic hydrogen.

Pauli: ojo cuando hay DOS electrones equivalentes



$m\backslash m_s$	1, 1/2	1,-1/2	0,1/2	0,-1/2	-1,1/2	-1,-1/2
1,1/2	NO					
1,-1/2	2 0	NO				
0, 1/2	1 1	1 0	NO			
0, -1/2	1 0	1 -1	0 0	NO		
-1, 1/2	0 1	0 0	-1 1	-1 0	NO	
-1, -1/2	0 0	0 -1	-1 0	-1 -1	-2 0	NO

Suma de momentos: contar



As an example, we count the states for each value of total m (z component quantum number) if we add $\ell_1 = 4$ to $\ell_2 = 2$.

audio

Total m	(m_1, m_2)
6	(4,2)
5	(3,2) (4,1)
4	(2,2) (3,1) (4,0)
3	(1,2) (2,1) (3,0) (4,-1)
2	(0,2) (1,1) (2,0) (3,-1) (4,-2)
1	(-1,2) (0,1) (1,0) (2,-1) (3,-2)
0	(-2,2) (-1,1) (0,0) (1,-1) (2,-2)
-1	(1,-2) (0,-1) (-1,0) (-2,1) (-3,2)
-2	(0,-2) (-1,-1) (-2,0) (-3,1) (-4,2)
-3	(-1,-2) (-2,-1) (-3,0) (-4,1)
-4	(-2,-2) (-3,-1) (-4,0)
-5	(-3,-2) (-4,-1)
-6	(-4,-2)

Since the highest m value is 6, we expect to have a $j = 6$ state which uses up one state for each m value from -6 to +6. Now the highest m value left is 5, so a $j = 5$ states uses up a state at each m value between -5 and +5. Similarly we find a $j = 4$, $j = 3$, and $j = 2$ state. This uses up all the states, and uses up the states at each value of m. So we find in this case,

$$|\ell_1 - \ell_2| \leq j \leq |\ell_1 + \ell_2|$$

and that j takes on every integer value between the limits. This makes sense in the vector model.

Interacción de espín-órbita

The **spin-orbit interaction** (between magnetic dipoles) will play a role in the fine structure of Hydrogen as well as in other problems. It is a good example of the need for states of total angular momentum. The additional term in the Hamiltonian is

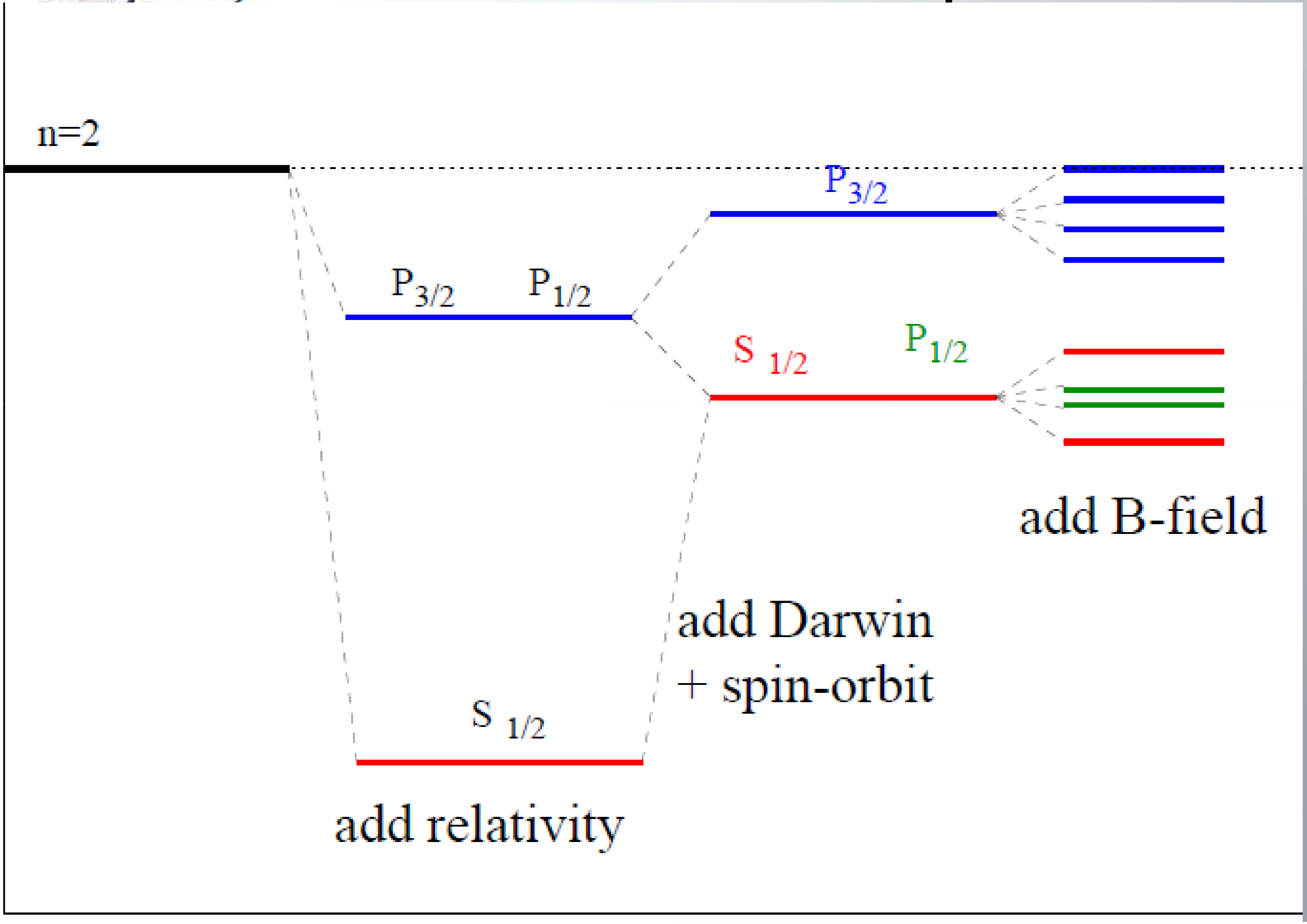
$$H_{SO} = \frac{Ze^2}{2m^2c^2}\frac{\vec{L}\cdot\vec{S}}{r^3}$$

f we define the **total angular momentum** $\vec{J}$ in the obvious way we can write $\vec{L}\cdot\vec{S}$ in terms of quantum numbers.

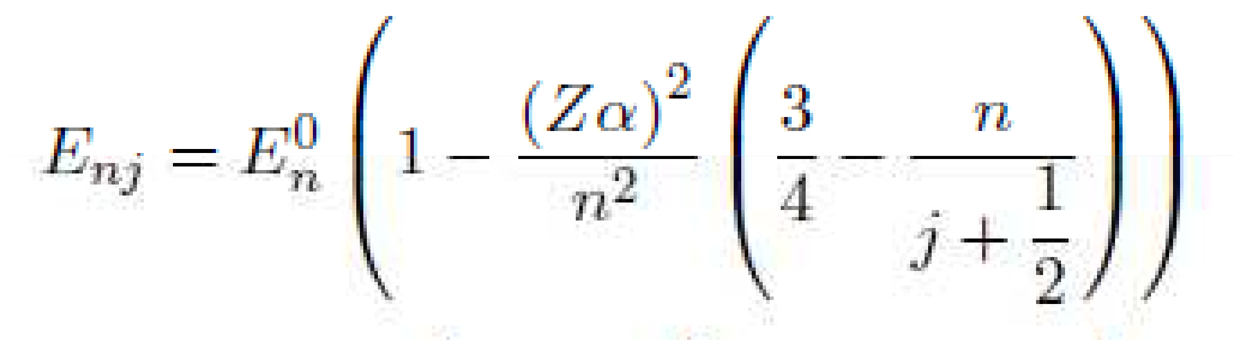
audio

$$\begin{aligned} \vec{J} &= \vec{L}+\vec{S} \\ J^2 &= L^2 + 2\vec{L}\cdot\vec{S} + S^2 \\ \vec{L}\cdot\vec{S} &= \frac{1}{2}(J^2 - L^2 - S^2) \rightarrow \frac{\hbar^2}{2}(j(j+1) - \ell(\ell+1) - s(s+1)) \end{aligned}$$

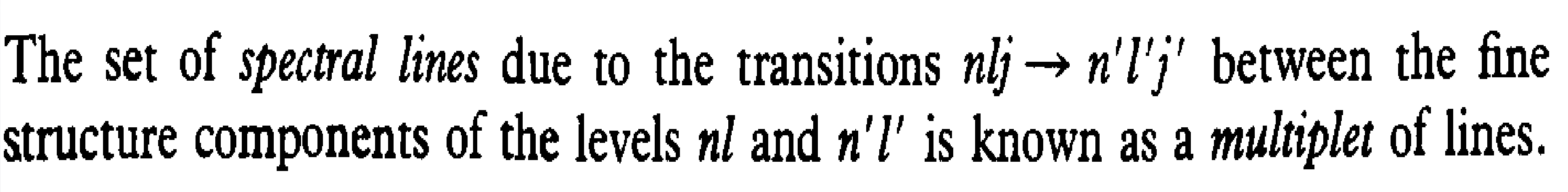
Interacción de espín-órbita



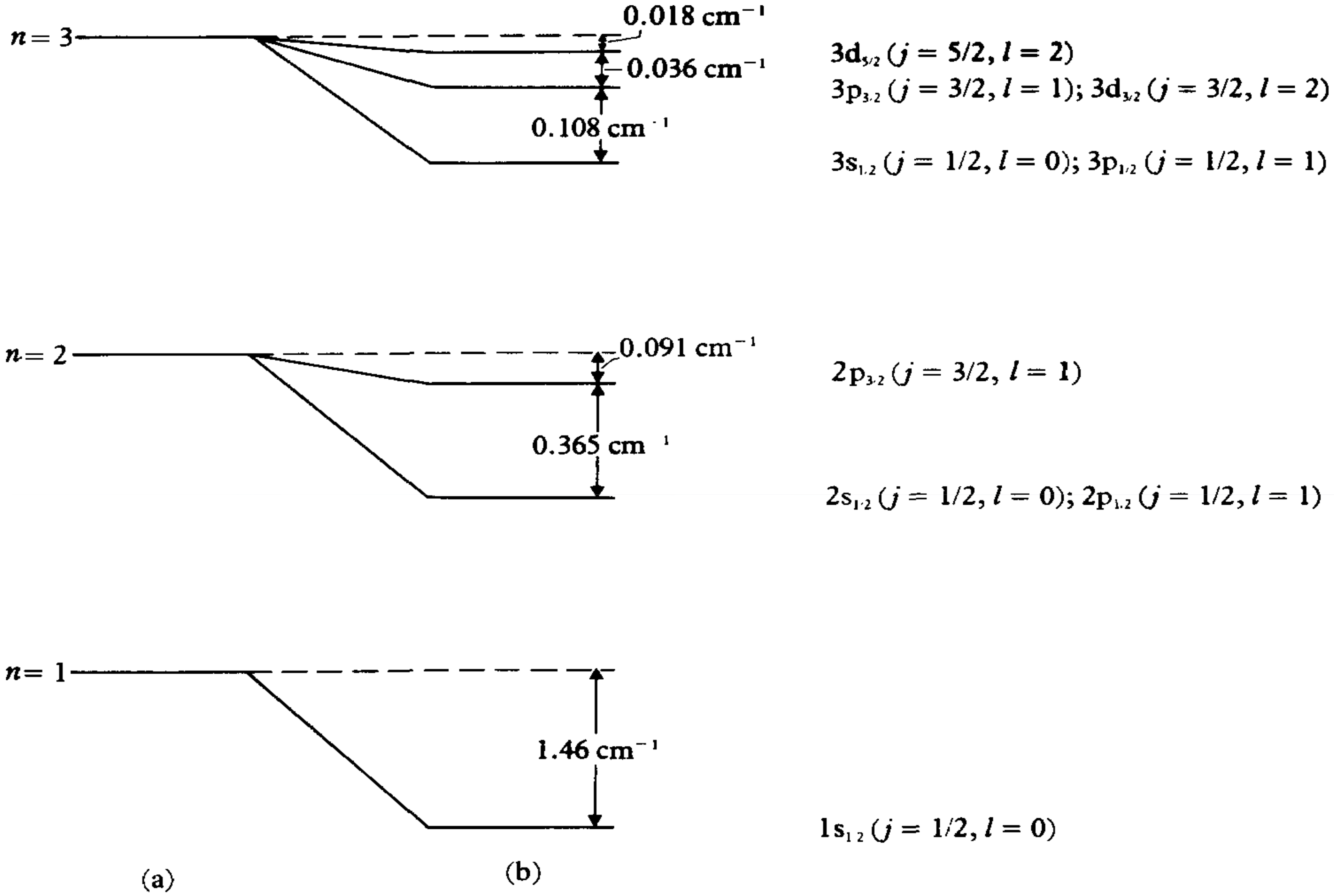
Niveles del átomo hidrogenoide con estructura fina



$$E_{nj} = E_n^0 \left(1 - \frac{(Z\alpha)^2}{n^2}\left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right)\right)$$



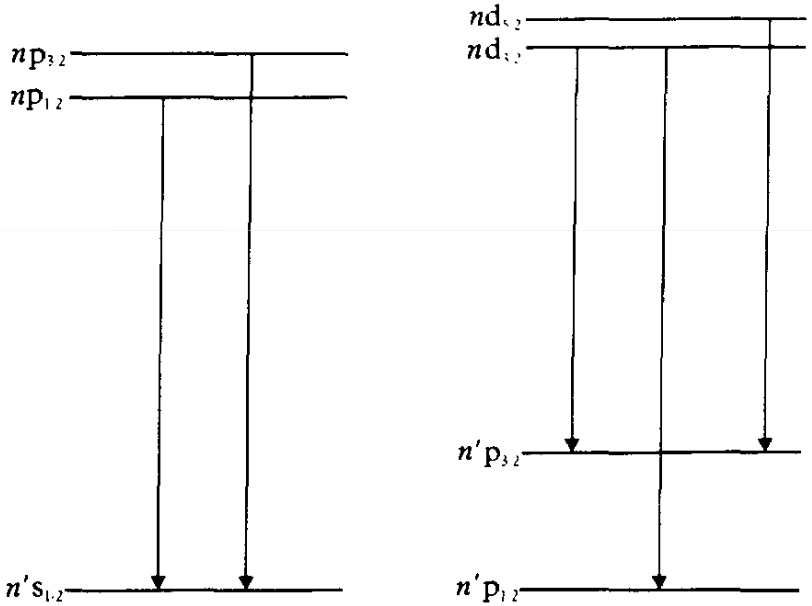
The set of *spectral lines* due to the transitions $nlj \rightarrow n'l'j'$ between the fine structure components of the levels nl and $n'l'$ is known as a *multiplet* of lines.



5.1 Fine structure of the hydrogen atom. The non-relativistic levels are shown on the left in column (a) and the split levels on the right in column (b), for $n = 1$, 2 and 3. For clarity, the scale in each diagram is different.

Balmer series (lower state $n = 2$) the following seven transitions are allowed:

$$n\mathrm{p}_{1/2}\text{–}2\mathrm{s}_{1/2}, \qquad n\mathrm{p}_{3/2}\text{–}2\mathrm{s}_{1/2}$$
$$n\mathrm{s}_{1/2}\text{–}2\mathrm{p}_{1/2}, \qquad n\mathrm{s}_{1/2}\text{–}2\mathrm{p}_{3/2}$$
$$n\mathrm{d}_{3/2}\text{–}2\mathrm{p}_{1/2}, \qquad n\mathrm{d}_{3/2}\text{–}2\mathrm{p}_{3/2},$$
$$n\mathrm{d}_{5/2}\text{–}2\mathrm{p}_{3/2}$$



(a) (b)

5.3 Allowed transitions in (a) the multiplet np –n's and (b) nd–n'p.

All the energy levels of the valence electron in an alkali (except for those with $l = 0$) are split into two; one level corresponding to a total angular momentum quantum number $j = l + 1/2$ and the other to $j = l - 1/2$. The interaction causing this splitting is the spin–orbit interaction, which was discussed in Chapter 5 in connection with the hydrogen atom. The shift in energy due to this effect is given by (see Section 5.1)

$$\Delta E = \tfrac{1}{2}\lambda_{nl}[j(j+1) - l(l+1) - \tfrac{3}{4}] \qquad [8.22]$$

The constant λ_{nl} is proportional to the expectation value of $r^{-1}\,\mathrm{d}V(r)/\mathrm{d}r$, $V(r)$ being the effective central potential in which the valence electron moves:

$$\lambda_{nl} = \frac{\hbar^2}{2m^2c^2}\left\langle \frac{1}{r}\frac{\mathrm{d}V(r)}{\mathrm{d}r} \right\rangle = \hbar^2\langle \xi(r) \rangle \qquad [8.23]$$

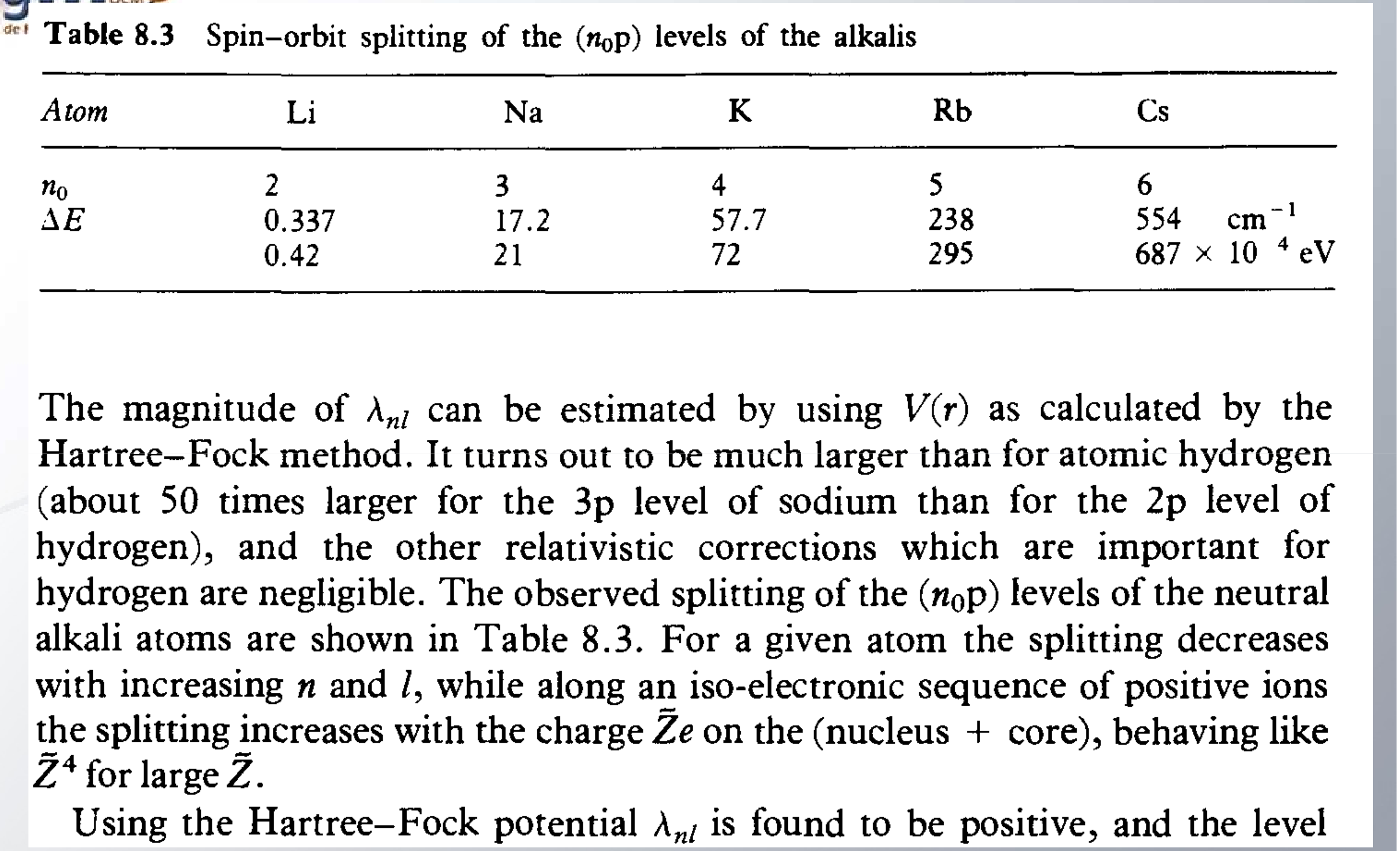


Table 8.3 Spin–orbit splitting of the (n_0p) levels of the alkalis

Atom	Li	Na	K	Rb	Cs	
n_0	2	3	4	5	6	
ΔE	0.337	17.2	57.7	238	554	cm^{-1}
	0.42	21	72	295	687	$\times 10^{4}$ eV

The magnitude of λ_{nl} can be estimated by using $V(r)$ as calculated by the Hartree–Fock method. It turns out to be much larger than for atomic hydrogen (about 50 times larger for the 3p level of sodium than for the 2p level of hydrogen), and the other relativistic corrections which are important for hydrogen are negligible. The observed splitting of the (n_0p) levels of the neutral alkali atoms are shown in Table 8.3. For a given atom the splitting decreases with increasing n and l, while along an iso-electronic sequence of positive ions the splitting increases with the charge $\tilde{Z}e$ on the (nucleus + core), behaving like $\tilde{Z}^4$ for large $\tilde{Z}$.

Using the Hartree–Fock potential λ_{nl} is found to be positive, and the level

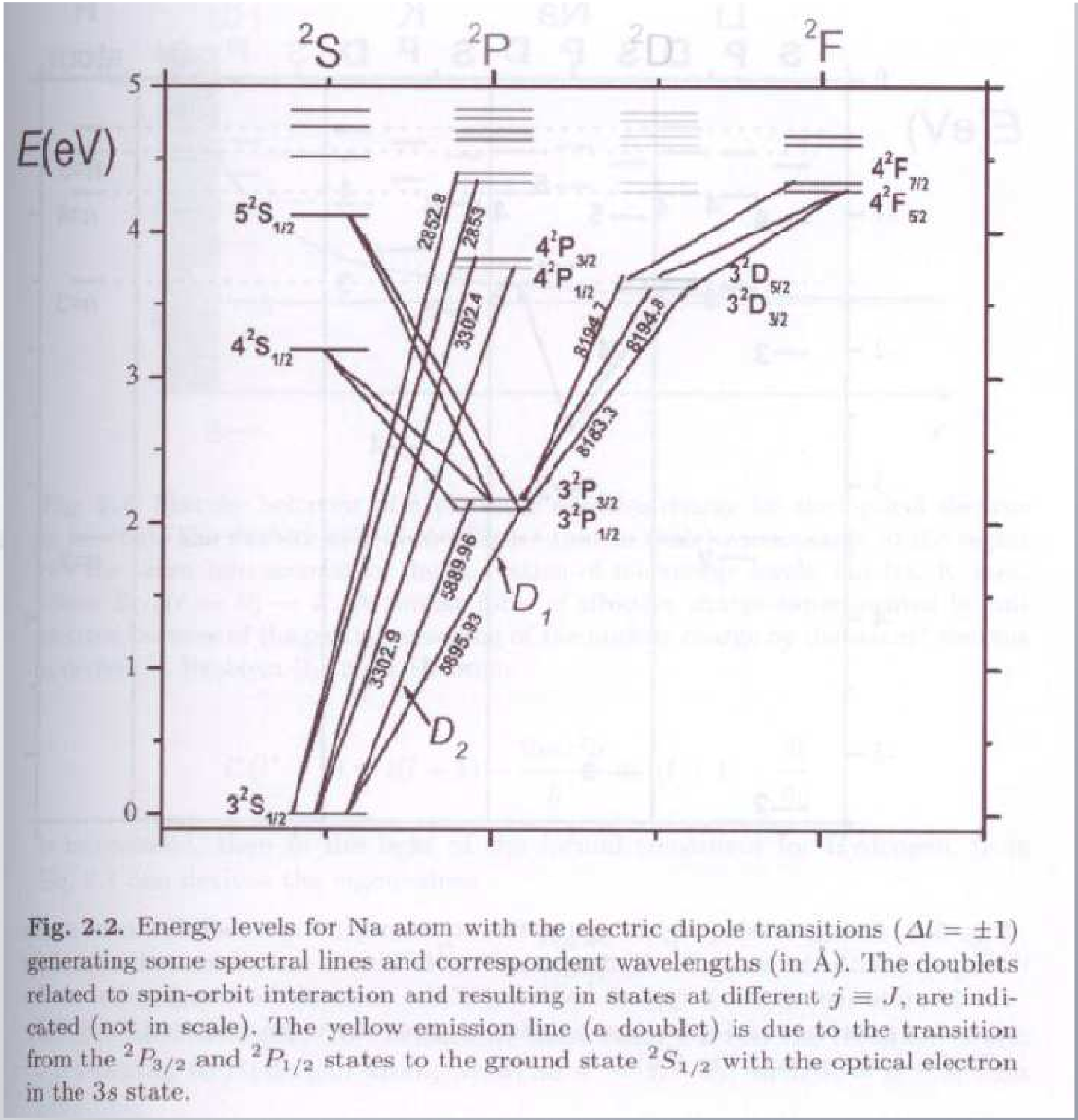
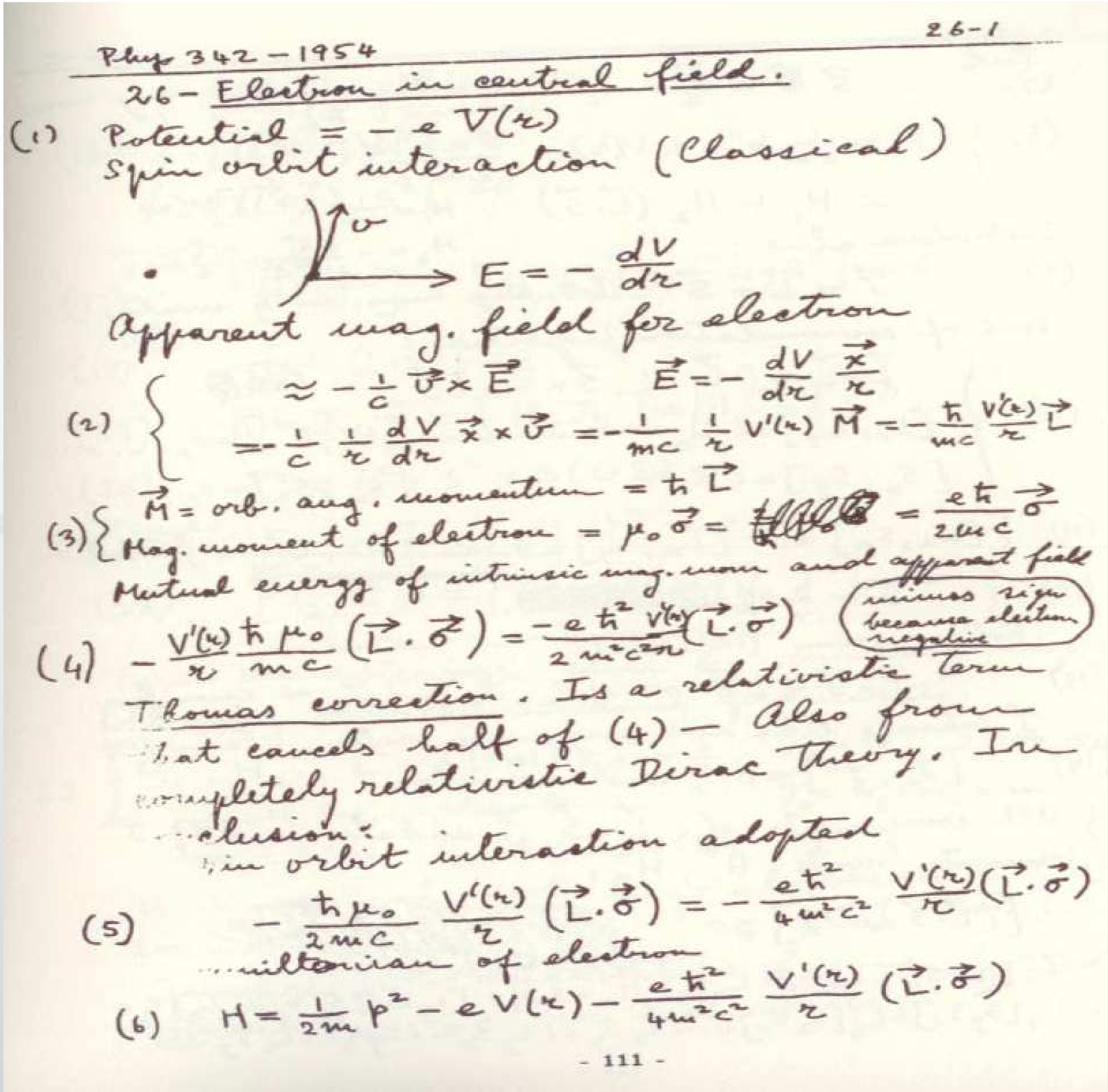


Fig. 2.2. Energy levels for Na atom with the electric dipole transitions ($\Delta l = \pm 1$) generating some spectral lines and correspondent wavelengths (in Å). The doublets related to spin-orbit interaction and resulting in states at different $j \equiv J$, are indicated (not in scale). The yellow emission line (a doublet) is due to the transition from the $^2P_{3/2}$ and $^2P_{1/2}$ states to the ground state $^2S_{1/2}$ with the optical electron in the $3s$ state.



Phy 342 — 1954

26 — Electron in central field.

(1) Potential $= -eV(r)$

Spin orbit interaction (Classical)

v $\qquad E = -\dfrac{dV}{dr}$

Apparent mag. field for electron

$$(2)\quad \begin{cases} \approx -\dfrac{1}{c}\vec{v}\times\vec{E} \qquad \vec{E} = -\dfrac{dV}{dr}\dfrac{\vec{x}}{r} \\ = -\dfrac{1}{c}\dfrac{1}{r}\dfrac{dV}{dr}\vec{x}\times\vec{v} = -\dfrac{1}{mc}\dfrac{1}{r}V'(r)\,\vec{M} = -\dfrac{\hbar}{mc}\dfrac{V'(r)}{r}\vec{L} \end{cases}$$

$$(3)\quad \begin{cases} \vec{M} = \text{orb. ang. momentum} = \hbar\vec{L} \\ \text{Mag. moment of electron} = \mu_0\vec{\sigma} = \text{[illegible]} = \dfrac{e\hbar}{2mc}\vec{\sigma} \end{cases}$$

Mutual energy of intrinsic mag. mom and apparent field

$$(4)\quad -\frac{V'(r)}{r}\frac{\hbar\mu_0}{mc}(\vec{L}\cdot\vec{\sigma}) = \frac{-e\hbar^2}{2m^2c^2r}V'(r)(\vec{L}\cdot\vec{\sigma})$$

minus sign because electron negative

Thomas correction. Is a relativistic term at cancels half of (4) — Also from mpletely relativistic Dirac theory. In

clusion:

in orbit interaction adopted

$$(5)\quad -\frac{\hbar\mu_0}{2mc}\frac{V'(r)}{r}(\vec{L}\cdot\vec{\sigma}) = -\frac{e\hbar^2}{4m^2c^2}\frac{V'(r)}{r}(\vec{L}\cdot\vec{\sigma})$$

miltonian of electron

$$(6)\quad H = \frac{1}{2m}p^2 - eV(r) - \frac{e\hbar^2}{4m^2c^2}\frac{V'(r)}{r}(\vec{L}\cdot\vec{\sigma})$$

Límite no relativista de la Ecuación de Dirac.

El objetivo de este ejercicio es obtener el límite no relativista de la Ecuación de Dirac que será la ecuación de Schrödinger.

La ecuación de Dirac es la siguiente:

$$\left[i\alpha\bar{\nabla} - \beta(M + Us) + E - Uv - Uc\right]\Psi = 0$$

Donde:

$$\alpha = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad \Psi = \begin{pmatrix} \Psi_{up} \\ \Psi_{down} \end{pmatrix}$$

Y σ son las matrices de Pauli.

A partir de la expresión matricial para α y para β se puede expresar la Ecuación de Dirac como un sistema de dos ecuaciones.

$$i\bar{\sigma}\cdot\bar{p}\Psi_{down} - (M + Us)\Psi_{up} + (E - Uv - Uc)\Psi_{up} = 0$$
$$i\bar{\sigma}\cdot\bar{p}\Psi_{up} + (M + Us)\Psi_{down} + (E - Uv - Uc)\psi_{down} = 0$$

Cambiando la notación para abreviar y teniendo en cuenta que p=-i$\bar{\nabla}$ se obtiene:

$$-\bar{\sigma}\cdot\bar{p}\Psi_{down} + A_{-}\Psi_{up} = 0$$
$$-\bar{\sigma}\cdot\bar{p}\Psi_{up} + A_{+}\Psi_{down} = 0$$

Donde:

$$A_{\pm} = \pm(M + Us) + (E - Us - Uc) \qquad \text{(son funciones de r)}$$

Multiplicando la segunda ecuación por $\bar{\sigma}\cdot\bar{p}$ se obtiene:

$$-(\bar{\sigma}\cdot\bar{p})(\bar{\sigma}\cdot\bar{p})\Psi_{up} + (\bar{\sigma}\cdot\bar{p})A_{+}\Psi_{down} = 0$$

Se obtiene:

$$\nabla^2\Psi_{up} + (\vec{\sigma}\cdot\vec{p})A_+\Psi_{down} = 0 \qquad \text{(A)}$$

Expresando en producto escalar $\vec{\sigma}\cdot\vec{p}$ como:

$$\vec{\sigma}\cdot\vec{p} = p_r\hat{r}\cdot\vec{\sigma} + p_\theta\hat{u}_\theta\cdot\vec{\sigma} + p_\phi\hat{u}_\phi\cdot\vec{\sigma}$$

Y expresando p_r como -i$\frac{\partial}{\partial r}$ se obtiene:

$$(\vec{\sigma}\cdot\vec{p})A_+\Psi_{down} = -i\hat{r}\cdot\vec{\sigma}\frac{\partial}{\partial r}\left[A_+\Psi_{down}\right] + (p_\theta\hat{u}_\theta\cdot\vec{\sigma} + p_\phi\hat{u}_\phi\cdot\vec{\sigma})A_+\Psi_{down}$$

Operando:

$$(\vec{\sigma}\cdot\vec{p})A_+\Psi_{down} = -i\hat{r}\cdot\vec{\sigma}\frac{\partial A_+}{\partial r}\Psi_{down} - i\hat{r}\cdot\vec{\sigma}A_+\frac{\partial\Psi_{down}}{\partial r} + (p_\theta\hat{u}_\theta\cdot\vec{\sigma} + p_\phi\hat{u}_\phi\cdot\vec{\sigma})A_+\Psi_{down} =$$

$$= -i\hat{r}\cdot\vec{\sigma}\frac{\partial A_+}{\partial r}\Psi_{down} + p_r\hat{r}\cdot\vec{\sigma}A_+\Psi_{down} + (p_\theta\hat{u}_\theta\cdot\vec{\sigma} + p_\phi\hat{u}_\phi\cdot\vec{\sigma})A_+\Psi_{down} =$$

$$= -i\hat{r}\cdot\vec{\sigma}\frac{\partial A_+}{\partial r}\Psi_{down} + A_+\mathrm{p}\cdot\boldsymbol{\sigma}\Psi_{\mathrm{down}}$$

Sustituyendo en (A) se obtiene:

$$\begin{aligned}\boldsymbol{\nabla}^2\Psi_{\mathrm{up}} = -\mathrm{p}\cdot\boldsymbol{\sigma}A_+\Psi_{\mathrm{down}} = i\boldsymbol{\sigma}\cdot\hat{\mathrm{r}}\left(\frac{dA_+}{dr}\right)\Psi_{\mathrm{down}} \\ -A_+\mathrm{p}\cdot\boldsymbol{\sigma}\Psi_{\mathrm{down}}\end{aligned} \qquad \text{(B)}$$

Despejando del sistema de ecuaciones inicial Ψ_{down} en términos de Ψ_{up} se puede obtener de la expresión (B) una ecuación para Ψ_{up}.

$$i\boldsymbol{\sigma}\cdot\hat{\mathrm{r}}\;\boldsymbol{\sigma}\cdot\mathrm{p}=\frac{d}{dr}-\frac{\boldsymbol{\sigma}\cdot\mathrm{l}}{r}\ ,$$

$$\left[\boldsymbol{\nabla}^2+\frac{1}{A_+}\frac{dA_+}{dr}\frac{\boldsymbol{\sigma}\cdot\mathrm{l}}{r}+A_+A_- -\frac{1}{A_+}\frac{dA_+}{dr}\frac{d}{dr}\right]\Psi_{\mathrm{up}}=0$$

Para eliminar la derivada primera, se hace la sustitución:

$$\Psi_{up}=A_+^{1/2}(r)\phi(\bar{r})$$

$$U_{\mathrm{DEB}}=V_{\mathrm{C}}+V_{\mathrm{so}}\boldsymbol{\sigma}\cdot\boldsymbol{l}$$

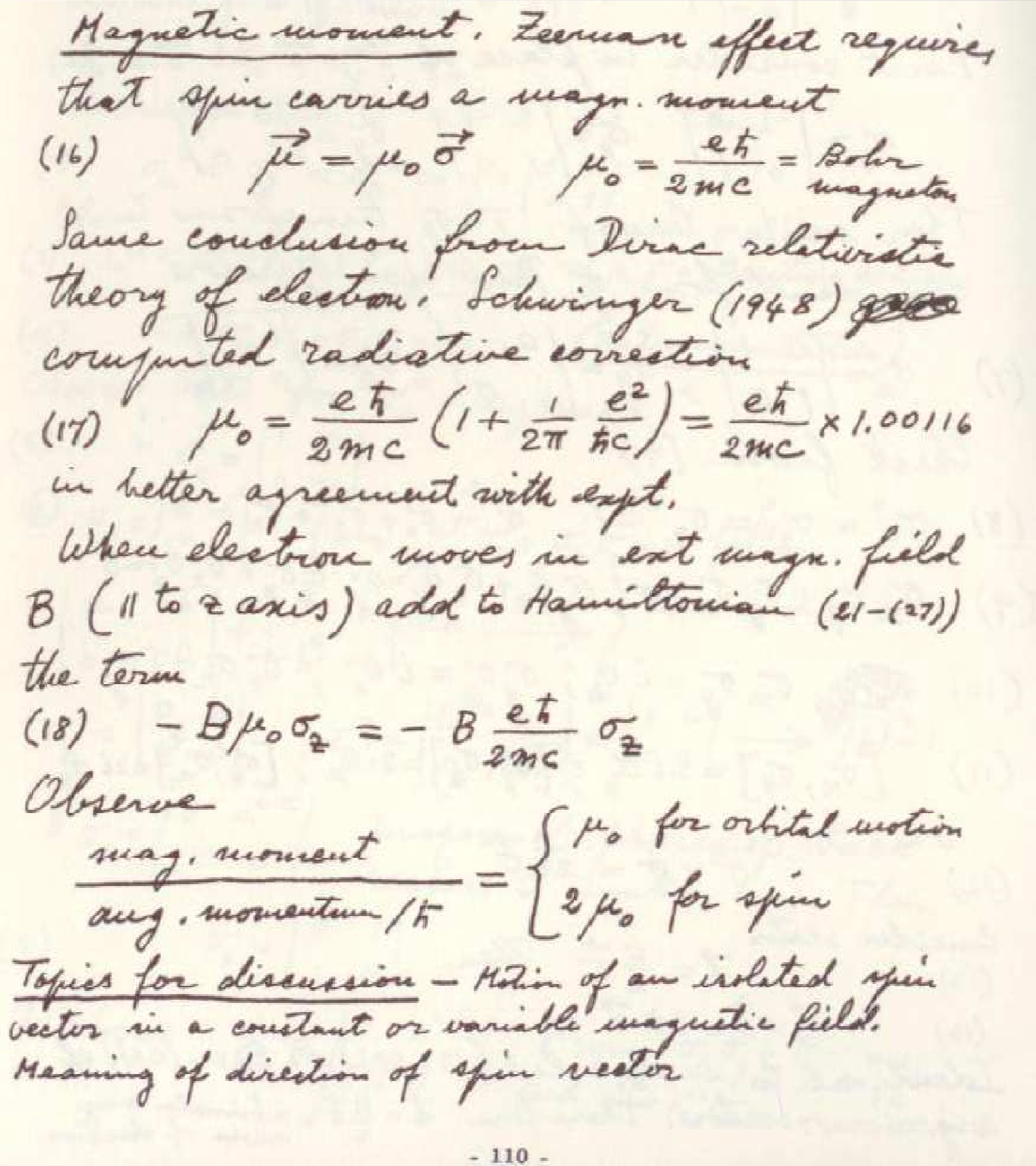
$$\left[-\frac{\boldsymbol{\nabla}^2}{2M}-U_{\mathrm{DEB}}\right]\phi(\mathbf{r})=E_{\mathrm{nr}}\phi(\mathbf{r})\ ,$$

$$V_{\mathrm{D}}=\frac{1}{rA}\frac{\partial A}{\partial r}+\frac{1}{2A}\frac{\partial^2 A}{\partial r^2}-\frac{3}{4A^2}\left(\frac{\partial A}{\partial r}\right)^2\ ,$$

$$V_{\mathrm{C}}=\frac{1}{2M}[(U_{\mathrm{V}}+U_{\mathrm{C}})^2-2E(U_{\mathrm{V}}+U_{\mathrm{C}})-U_{\mathrm{S}}^2$$
$$-2MU_{\mathrm{S}}+V_{\mathrm{D}}]\ ,$$

$$A(r)=\frac{E-U_{\mathrm{V}}-U_{\mathrm{C}}+M+U_{\mathrm{S}}}{E+M}\ ,$$

$$V_{\mathrm{so}}=\frac{1}{2M}\frac{1}{rA}\frac{\partial A}{\partial r}\ .$$



Magnetic moment. Zeeman effect requires that spin carries a magn. moment

(16) $$\vec{\mu} = \mu_0 \vec{\sigma} \qquad \mu_0 = \frac{e\hbar}{2mc} = \text{Bohr magneton}$$

Same conclusion from Dirac relativistic theory of electron. Schwinger (1948) computed radiative correction

(17) $$\mu_0 = \frac{e\hbar}{2mc}\left(1 + \frac{1}{2\pi}\frac{e^2}{\hbar c}\right) = \frac{e\hbar}{2mc} \times 1.00116$$

in better agreement with expt.

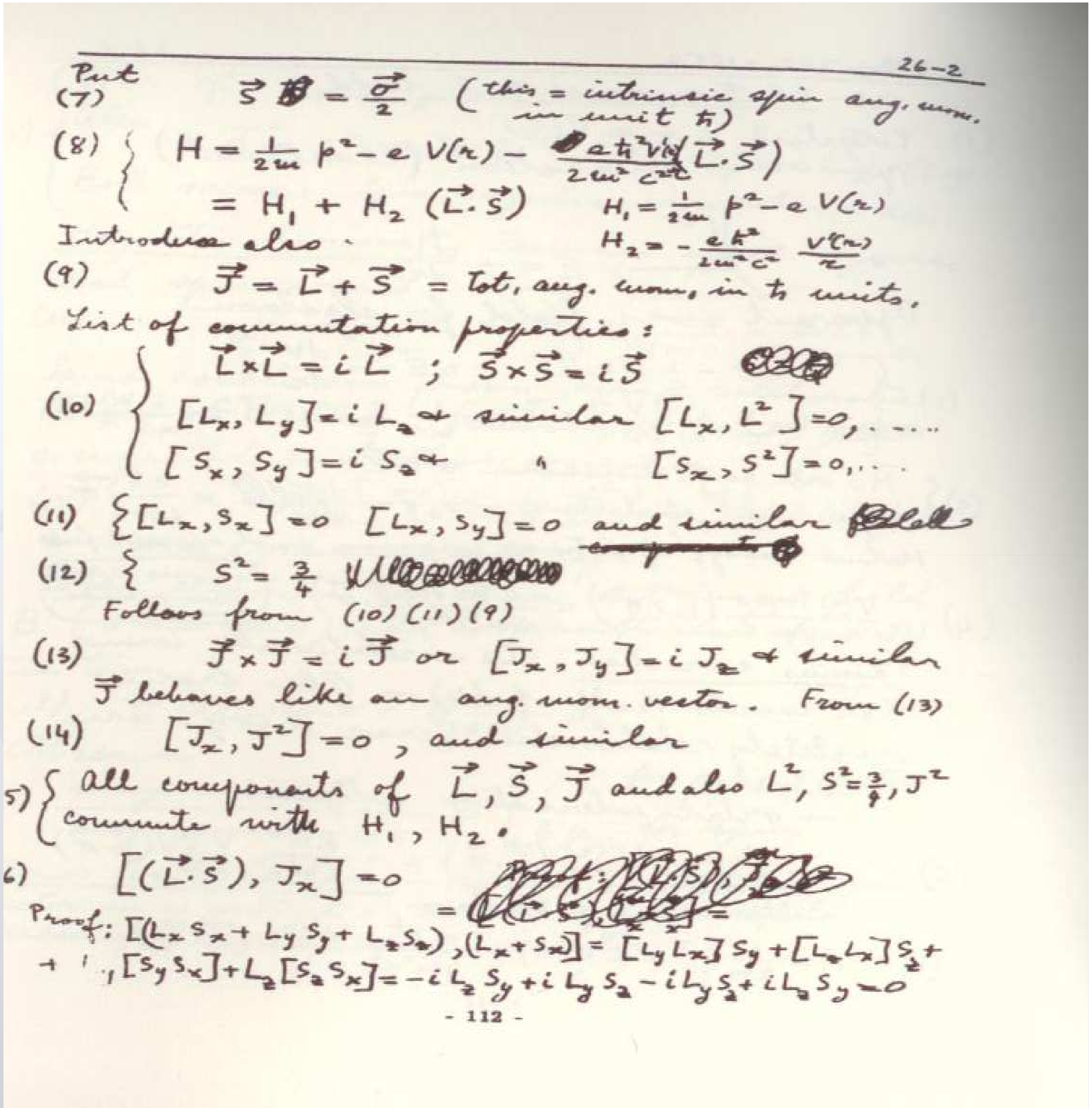
When electron moves in ext magn. field B (∥ to z axis) add to Hamiltonian (21-(27)) the term

(18) $$-B\mu_0\sigma_z = -B\frac{e\hbar}{2mc}\sigma_z$$

Observe

$$\frac{\text{mag. moment}}{\text{ang. momentum}/\hbar} = \begin{cases} \mu_0 & \text{for orbital motion} \\ 2\mu_0 & \text{for spin} \end{cases}$$

Topics for discussion — Motion of an isolated spin vector in a constant or variable magnetic field. Meaning of direction of spin vector



Put

(7) $\vec S = \frac{\vec\sigma}{2}$ (this = intrinsic spin ang. mom. in unit $\hbar$)

(8) $$\begin{cases} H = \frac{1}{2m}p^2 - eV(r) - \frac{e\hbar^2 V'(r)}{2m^2c^2 r}(\vec L\cdot\vec S) \\ \quad = H_1 + H_2\,(\vec L\cdot\vec S) \end{cases}$$ $H_1 = \frac{1}{2m}p^2 - eV(r)$

$H_2 = -\frac{e\hbar^2}{2m^2c^2}\frac{V'(r)}{r}$

Introduce also .

(9) $\vec J = \vec L + \vec S$ = tot. ang. mom. in $\hbar$ units.

List of commutation properties:

(10) $$\begin{cases} \vec L \times \vec L = i\vec L \; ; \; \vec S\times\vec S = i\vec S \\ [L_x, L_y] = i L_z \text{ \& similar } [L_x, L^2] = 0, \ldots \\ [S_x, S_y] = i S_z \text{ \& } \quad \text{"} \quad [S_x, S^2] = 0, \ldots \end{cases}$$

(11) $\{[L_x, S_x] = 0 \quad [L_x, S_y] = 0$ and similar ~~components~~

(12) $\{ \quad S^2 = \frac{3}{4}$

Follows from (10) (11) (9)

(13) $\vec J \times \vec J = i\vec J$ or $[J_x, J_y] = i J_z$ & similar

$\vec J$ behaves like an ang. mom. vector. From (13)

(14) $[J_x, J^2] = 0$, and similar

5) $\{$ all components of $\vec L, \vec S, \vec J$ and also $L^2, S^2 = \frac{3}{4}, J^2$ commute with H_1, H_2.

6) $[(\vec L\cdot\vec S), J_x] = 0$

Proof: $[(L_xS_x + L_yS_y + L_zS_z), (L_x + S_x)] = [L_yL_x]S_y + [L_zL_x]S_z +$

$+$ ' , $[S_yS_x] + L_z[S_zS_x] = -iL_zS_y + iL_yS_z - iL_yS_z + iL_zS_y = 0$

$$(16)\begin{cases}[(\vec{L}\cdot\vec{S}),J^2]=0\\ [(\vec{L}\cdot\vec{S}),L^2]=0\\ [(\vec{L}\cdot\vec{S}),S^2]=0\end{cases}$$

Therefore

$$(17)\quad [H,J^2]=[H,L^2]=[H,S^2]=0$$

also

$$(18)\quad [H,(L\cdot S)]=0$$

$$(19)\quad [H,J_x]=[H,J_y]=[H,J_z]=0$$

$$(20)\quad J^2=L^2+S^2+2(L\cdot S)$$

Hence

$$(21)\quad [J^2,L^2]=[J^2,S^2]=0$$

$$(22)\quad [J_z,L^2]=[J_z,S^2]=[J_z,J^2]=0$$

First characterize state by making diagon
following intercommuting quantities

$$23\begin{cases}H_1,\ H_2,\ L^2=l(l+1),\ S^2=\frac{3}{4},\ L_z=m_l,\ S_z=m_s \qquad J_z=m_l+m_s=m\\ m_l=l,l-1,\ldots,-l+1,-l\\ m_s=\pm 1/2 \qquad l-\frac{1}{2}\le J_z\le l+\frac{1}{2}\end{cases}$$

H in general <u>not</u> diagonal because $(L\cdot S)$
does not commute with L_z or S_z. But $[(L\cdot S),$
Therefore $(L\cdot S)$ mixes states of same $J_z=m$
different L_z, S_z. Two such states:

$$(24)\begin{cases}L_z=m-\frac{1}{2},\ S_z=\frac{1}{2}\quad \text{state } |m-\frac{1}{2},\frac{1}{2}\rangle\\ \text{and}\\ L_z=m+\frac{1}{2}\quad S_z=-\frac{1}{2}\quad \text{state } |m+\frac{1}{2},\frac{1}{2}\rangle\\ |m-\frac{1}{2},\frac{1}{2}\rangle = \psi_{m-\frac{1}{2},\frac{1}{2}}=f(r)\,Y_{l,m-\frac{1}{2}}\begin{vmatrix}1\\0\end{vmatrix}\\ |m+\frac{1}{2},\frac{-1}{2}\rangle = \psi_{m+\frac{1}{2},\frac{1}{2}}=f(r)\,Y_{l,m+\frac{1}{2}}\begin{vmatrix}0\\1\end{vmatrix}\end{cases}$$

Find from Lects (18 especially (17) (18)) and

$$(25)\begin{cases}\text{Lect (25)}\\ \text{use}\end{cases}\quad S_x+iS_y=\begin{vmatrix}0&1\\0&0\end{vmatrix}\quad S_x-iS_y=\begin{vmatrix}0&0\\1&0\end{vmatrix}\quad S_z=\begin{vmatrix}1&0\\0&-1\end{vmatrix}$$

$$(26)\ \{\ (L\cdot S)=\frac{1}{2}(L_x+iL_y)(S_x-iS_y)+\frac{1}{2}(L_x-iL_y)(S_x+iS_y)+L_zS_z$$

$$(27)\begin{cases}(L_x+iL_y)\,Y_{l,m-\frac{1}{2}}=\sqrt{(l+\frac{1}{2})^2-m^2}\;Y_{l,m+\frac{1}{2}}\\ (L_x-iL_y)\,Y_{l,m+\frac{1}{2}}=\sqrt{(l+\frac{1}{2})^2-m^2}\;Y_{l,m-\frac{1}{2}}\end{cases}$$

$m\pm\frac{1}{2}$ = integral number

$$(28)\begin{cases}(S_x+iS_y)\begin{vmatrix}1\\0\end{vmatrix}=0\quad (S_x+iS_y)\begin{vmatrix}0\\1\end{vmatrix}=\begin{vmatrix}1\\0\end{vmatrix}\\ (S_x-iS_y)\begin{vmatrix}0\\1\end{vmatrix}=0\quad (S_x-iS_y)\begin{vmatrix}1\\0\end{vmatrix}=\begin{vmatrix}0\\1\end{vmatrix}\end{cases}$$

<u>Find</u>

$$(29)\begin{cases}(L\cdot S)\,|m-\frac{1}{2},\frac{1}{2}\rangle=\frac{1}{2}(m-\frac{1}{2})|m-\frac{1}{2},\frac{1}{2}\rangle+\frac{1}{2}\sqrt{(l+\frac{1}{2})^2-m^2}\,|m+\frac{1}{2},\frac{-1}{2}\rangle\\ (L\cdot S)\,|m+\frac{1}{2},-\frac{1}{2}\rangle=\frac{1}{2}\sqrt{(l+\frac{1}{2})^2-m^2}\,|m-\frac{1}{2},\frac{1}{2}\rangle-\frac{1}{2}(m+\frac{1}{2})|m+\frac{1}{2},\frac{-1}{2}\rangle\end{cases}$$

$$(30)\quad (L\cdot S)=\begin{Vmatrix}\frac{1}{2}(m-\frac{1}{2}), & \frac{1}{2}\sqrt{(l+1/2)^2-m^2}\\ \frac{1}{2}\sqrt{(l+1/2)^2-m^2}, & -\frac{1}{2}(m+\frac{1}{2})\end{Vmatrix}$$

e.v's of $(\vec{L}\cdot\vec{S})$ & corresp e.f's are

$$(31)\quad\begin{cases}\vec{L}\cdot\vec{S} = \frac{1}{2}\ell \text{ with e.f (normalized)} \\ \sqrt{\frac{1}{2}+\frac{m}{2\ell+1}}\,\left|m-\frac{1}{2},\frac{1}{2}\right\rangle + \sqrt{\frac{1}{2}-\frac{m}{2\ell+1}}\,\left|m+\frac{1}{2},\frac{-1}{2}\right\rangle\end{cases}$$

and

$$(32)\quad\begin{cases}\vec{L}\cdot\vec{S} = -\frac{1}{2}(\ell+1) \text{ with normalized e.f.} \\ -\sqrt{\frac{1}{2}-\frac{m}{2\ell+1}}\,\left|m-\frac{1}{2},\frac{1}{2}\right\rangle + \sqrt{\frac{1}{2}+\frac{m}{2\ell+1}}\,\left|m+\frac{1}{2},\frac{-1}{2}\right\rangle\end{cases}$$

E.v's of J^2 from (20) (31) (32)

$$(33)\quad\begin{cases}\text{for } LS = \frac{\ell}{2},\ J^2 = \ell(\ell+1)+\frac{3}{4}+\ell = (\ell+\frac{1}{2})(\ell+\frac{1}{2}+1) \\ s \parallel \text{to } \ell \text{ or vector model},\ J = \ell+\frac{1}{2} \\ \vec{J}^2 = J(J+1).\ \text{E.f is (31).}\end{cases}$$

$$(34)\quad\begin{cases}\text{for } LS = -\frac{1}{2}(\ell+1),\ J^2 = \ell(\ell+1)+\frac{3}{4}-\ell-1 = (\ell-\frac{1}{2})(\ell+\frac{1}{2}) \\ \text{Spin antiparallel to } \ell,\ J = \ell-\frac{1}{2} \qquad \vec{J}^2 = J(J+1) = \ell^2-\frac{1}{4} \\ \text{E.f is (32).}\end{cases}$$

<u>Doublet splitting of energy levels.</u> From (8)

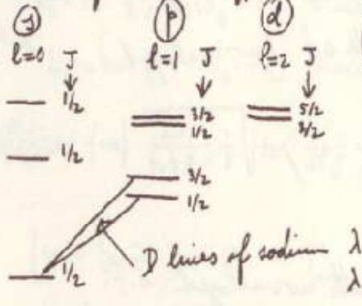
$$(35)\quad -\frac{e\hbar^2}{2m^2c^2}\frac{V'(r)}{r}(L\cdot S)$$ treated as perturbation, yields energy perturbation

this, usually, positive ↙

R_ℓ = radial wave function ↙

$$(36)\quad \delta E = \frac{e\hbar^2}{2m^2c^2}\left(\int\left\{V'(r)\right\}R_\ell^2(r)\,r\,dr\right)\times\begin{cases}\ell/2 & \text{for } J=\ell+\frac{1}{2} \\ \text{or} & \\ -(\ell+1)/2 & \text{for } J=\ell-\frac{1}{2}\end{cases}$$

Doublet spectrum (Typical case Alkali atoms)



Notation
$s_{1/2}, p_{1/2}, p_{3/2}, d_{3/2}, d_{5/2}$

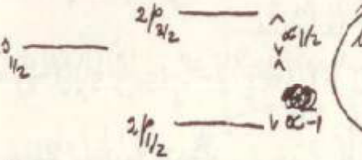
D lines of sodium $\lambda = 5890$ Å and
$\lambda = 5896$ Å

Case of $n = 2$ levels of hydrogen. From lect. 8

$$E = -\frac{me^4}{2\hbar^2 \times 2^2} \text{ for } 2s + 2p \text{ levels.}$$

Spin perturbation (36) $(\delta_1 E)$

(37) $\delta_1 E(2s) = 0 \qquad \delta_1 E(2p) = \frac{e^2\hbar^2}{48 m^2 c^2}\frac{1}{a^3}\begin{cases} 1/2 \\ -1 \end{cases}$



Use $R_{2p} = \frac{r\, e^{-r/2a}}{\sqrt{24a^5}}$
and $V = \frac{e}{r}$ in (36)

Relativity perturbation $(\delta_2 E)$

(38) $\text{kin. energy} = \sqrt{m^2c^4 + c^2p^2} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$

(39) $\text{Perturbation} = -\frac{1}{8m^3c^2}\, p^4 = -\frac{\hbar^4}{8m^3c^2}(\nabla^2)^2$

(40) One finds using first approx. perturbation theory

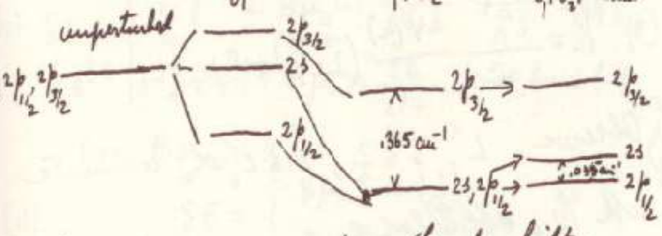
$\delta_2 E(2s) = -\frac{5}{128}\frac{e^8 m}{\hbar^4 c^2} \qquad \delta_2 E(2p) = -\frac{7}{384}\frac{e^8 m}{\hbar^4 c^2}$

(See for general formulas: Schiff p. 325, 326)

$\delta_1(E_{2s}) + \delta_2(E_{2s}) = -\frac{5}{128}\frac{e^8 m}{\hbar^4 c^2}$ ← !!

$\delta_1(E_{2p_{1/2}}) + \delta_2(E_{2p_{1/2}}) = \left(-\frac{1}{48} - \frac{7}{384}\right)\frac{e^8 m}{\hbar^4 c^2} = -\frac{5}{128}\frac{e^8 m}{\hbar^4 c^2}$

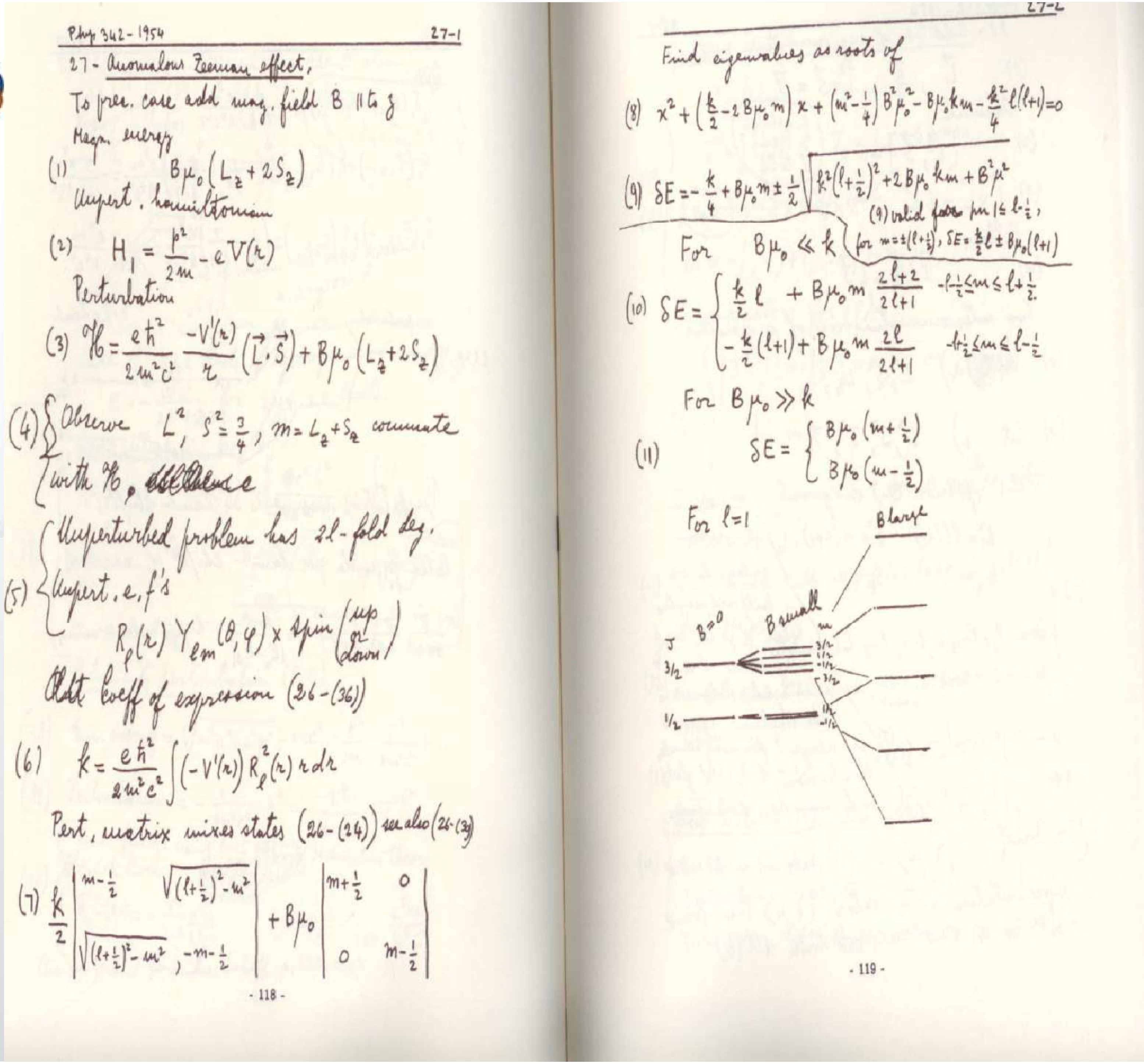
$\delta_1(E_{2p_{3/2}}) + \delta_2(E_{2p_{3/2}}) = \left(\frac{1}{96} - \frac{7}{384}\right)\frac{e^8 m}{\hbar^4 c^2} = -\frac{1}{128}\frac{e^8 m}{\hbar^4 c^2}$



Qualitative comments on Lamb shift;

Bethe formula for Lamb shift of ns-levels

$$\frac{8}{3\pi n^3}\frac{me^4}{2\hbar^2}\left(\frac{e^2}{\hbar c}\right)^3 \overline{\ln\frac{mc^2}{|E_n - E_s|}} + \text{higher order corrections}$$



27 - Anomalous Zeeman effect,

To prec. case add mag. field B ‖ to z

Magn. energy

(1) $$B\mu_0\left(L_z+2S_z\right)$$

Unpert. hamiltonian

(2) $$H_1=\frac{p^2}{2m}-eV(r)$$

Perturbation

(3) $$\mathcal{H}=\frac{e\hbar^2}{2m^2c^2}\,\frac{-V'(r)}{r}\left(\vec{L}\cdot\vec{S}\right)+B\mu_0\left(L_z+2S_z\right)$$

(4) Observe L^2, $S^2=\frac{3}{4}$, $m=L_z+S_z$ commute with $\mathcal{H}$, ~~[illegible]~~

(5) Unperturbed problem has $2l$-fold deg. Unpert. e. f's

$$R_l(r)\,Y_{lm}(\theta,\varphi)\times\text{spin}\begin{pmatrix}\text{up}\\ \text{or}\\ \text{down}\end{pmatrix}$$

Obt. coeff of expression (26-(36))

(6) $$k=\frac{e\hbar^2}{2m^2c^2}\int\left(-V'(r)\right)R_l^2(r)\,r\,dr$$

Pert. matrix mixes states (26-(24)) see also (26-(39)

(7) $$\frac{k}{2}\begin{vmatrix} m-\frac{1}{2} & \sqrt{\left(l+\frac{1}{2}\right)^2-m^2}\\ \sqrt{\left(l+\frac{1}{2}\right)^2-m^2}, & -m-\frac{1}{2}\end{vmatrix}+B\mu_0\begin{vmatrix} m+\frac{1}{2} & 0\\ 0 & m-\frac{1}{2}\end{vmatrix}$$

Find eigenvalues as roots of

(8) $$x^2+\left(\frac{k}{2}-2B\mu_0 m\right)x+\left(m^2-\frac{1}{4}\right)B^2\mu_0^2-B\mu_0 km-\frac{k^2}{4}l(l+1)=0$$

(9) $$\delta E=-\frac{k}{4}+B\mu_0 m\pm\frac{1}{2}\sqrt{k^2\left(l+\frac{1}{2}\right)^2+2B\mu_0 km+B^2\mu^2}$$

(9) valid for $|m|\le l-\frac{1}{2}$, for $m=\pm\left(l+\frac{1}{2}\right)$, $\delta E=\frac{k}{2}l\pm B\mu_0(l+1)$

For $B\mu_0\ll k$

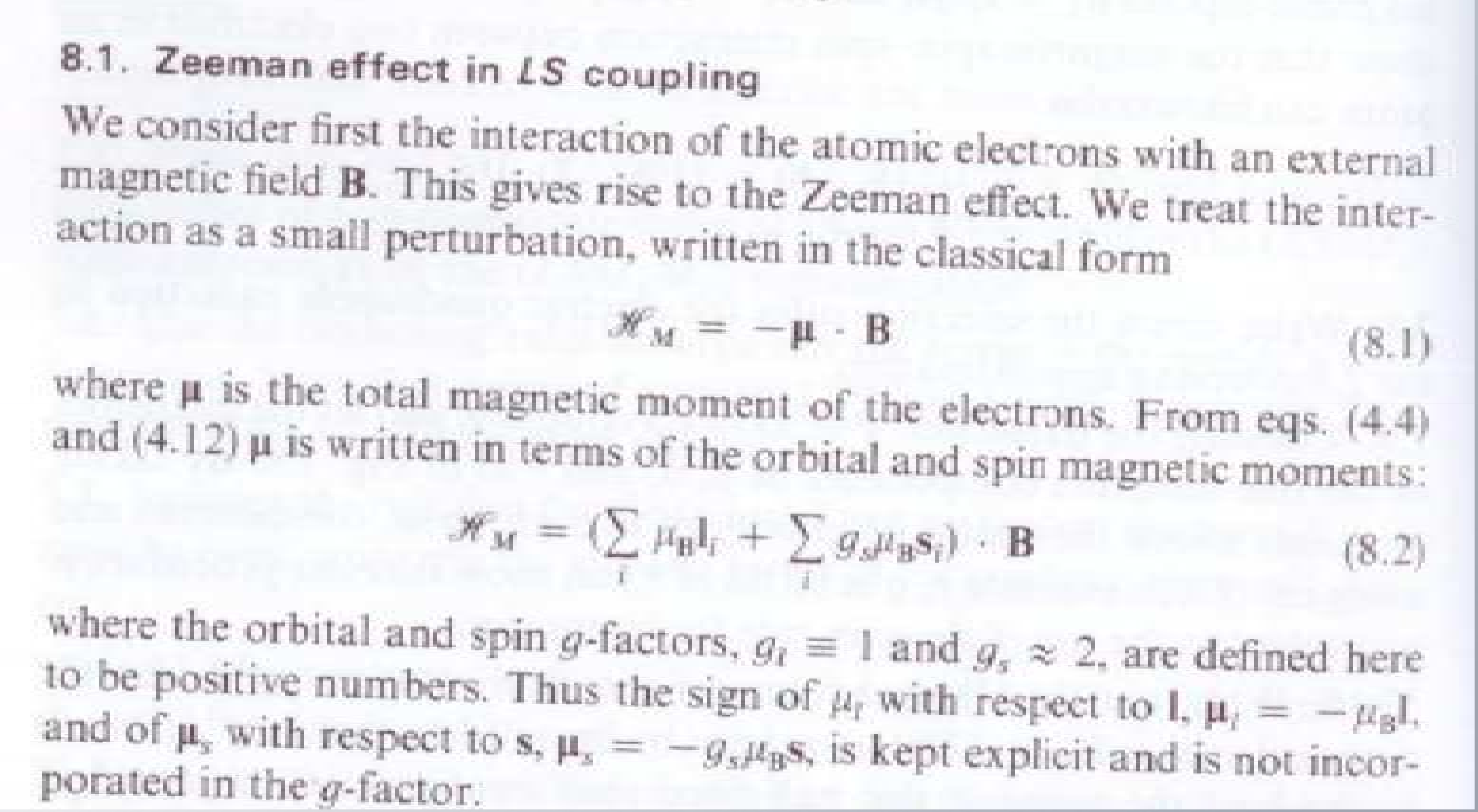
(10) $$\delta E=\begin{cases}\frac{k}{2}l+B\mu_0 m\,\frac{2l+2}{2l+1} & -l-\frac{1}{2}\le m\le l+\frac{1}{2}\\ -\frac{k}{2}(l+1)+B\mu_0 m\,\frac{2l}{2l+1} & -l+\frac{1}{2}\le m\le l-\frac{1}{2}\end{cases}$$

For $B\mu_0\gg k$

(11) $$\delta E=\begin{cases}B\mu_0\left(m+\frac{1}{2}\right)\\ B\mu_0\left(m-\frac{1}{2}\right)\end{cases}$$

For $l=1$

Efecto Zeeman



8.1. Zeeman effect in *LS* coupling

We consider first the interaction of the atomic electrons with an external magnetic field **B**. This gives rise to the Zeeman effect. We treat the interaction as a small perturbation, written in the classical form

$$\mathscr{H}_M = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{8.1}$$

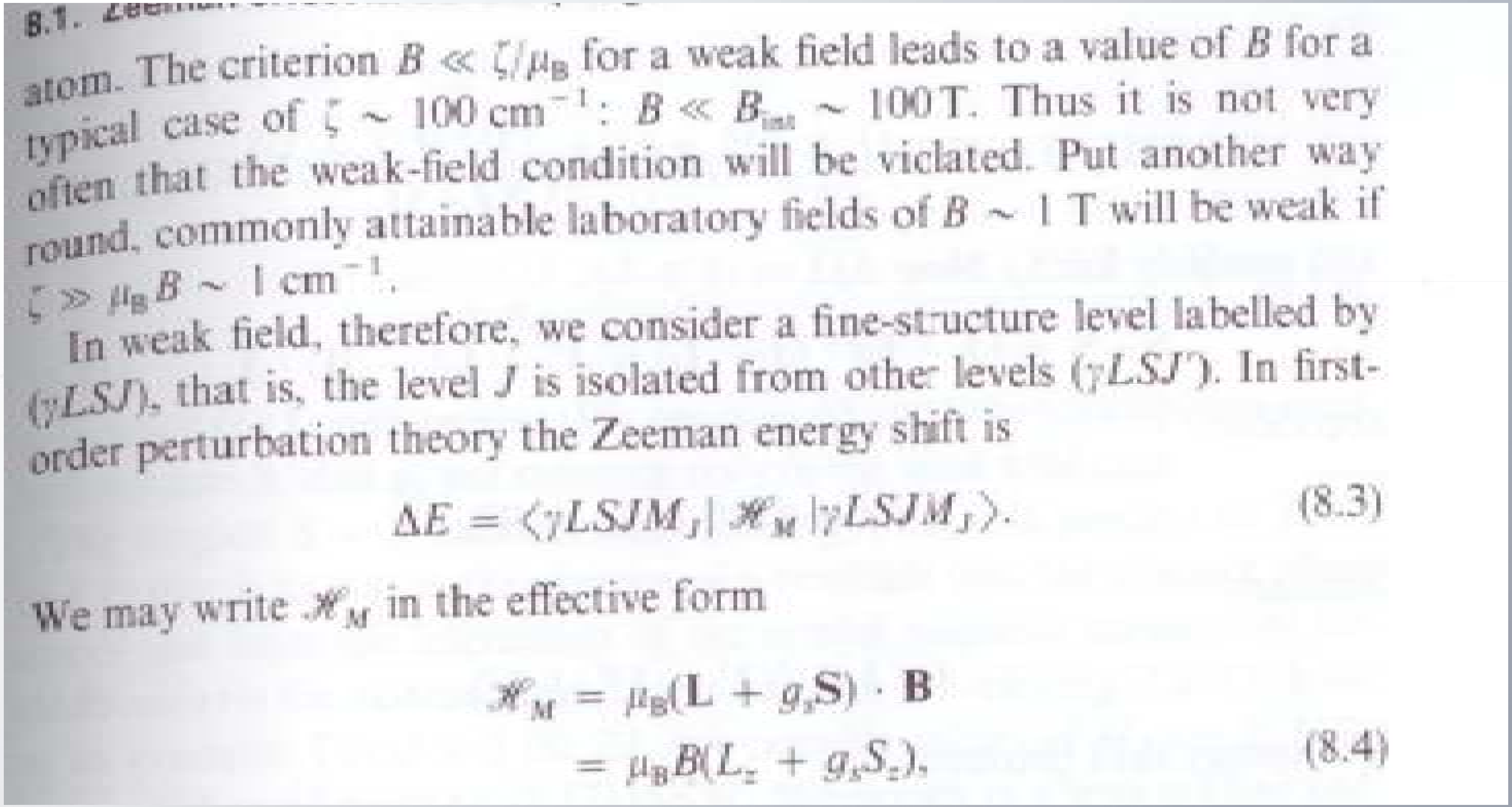
where $\boldsymbol{\mu}$ is the total magnetic moment of the electrons. From eqs. (4.4) and (4.12) $\boldsymbol{\mu}$ is written in terms of the orbital and spin magnetic moments:

$$\mathscr{H}_M = \Big(\sum_i \mu_B \mathbf{l}_i + \sum_i g_s \mu_B \mathbf{s}_i\Big) \cdot \mathbf{B} \tag{8.2}$$

where the orbital and spin g-factors, $g_l \equiv 1$ and $g_s \approx 2$, are defined here to be positive numbers. Thus the sign of μ_l with respect to $\mathbf{l}$, $\boldsymbol{\mu}_l = -\mu_B \mathbf{l}$, and of $\boldsymbol{\mu}_s$ with respect to $\mathbf{s}$, $\boldsymbol{\mu}_s = -g_s \mu_B \mathbf{s}$, is kept explicit and is not incorporated in the g-factor.

Efecto Zeeman

Sucede cuando el hamiltoniano incluye un campo magnético ‘débil’, comparado con el término de espín-órbita



8.1.

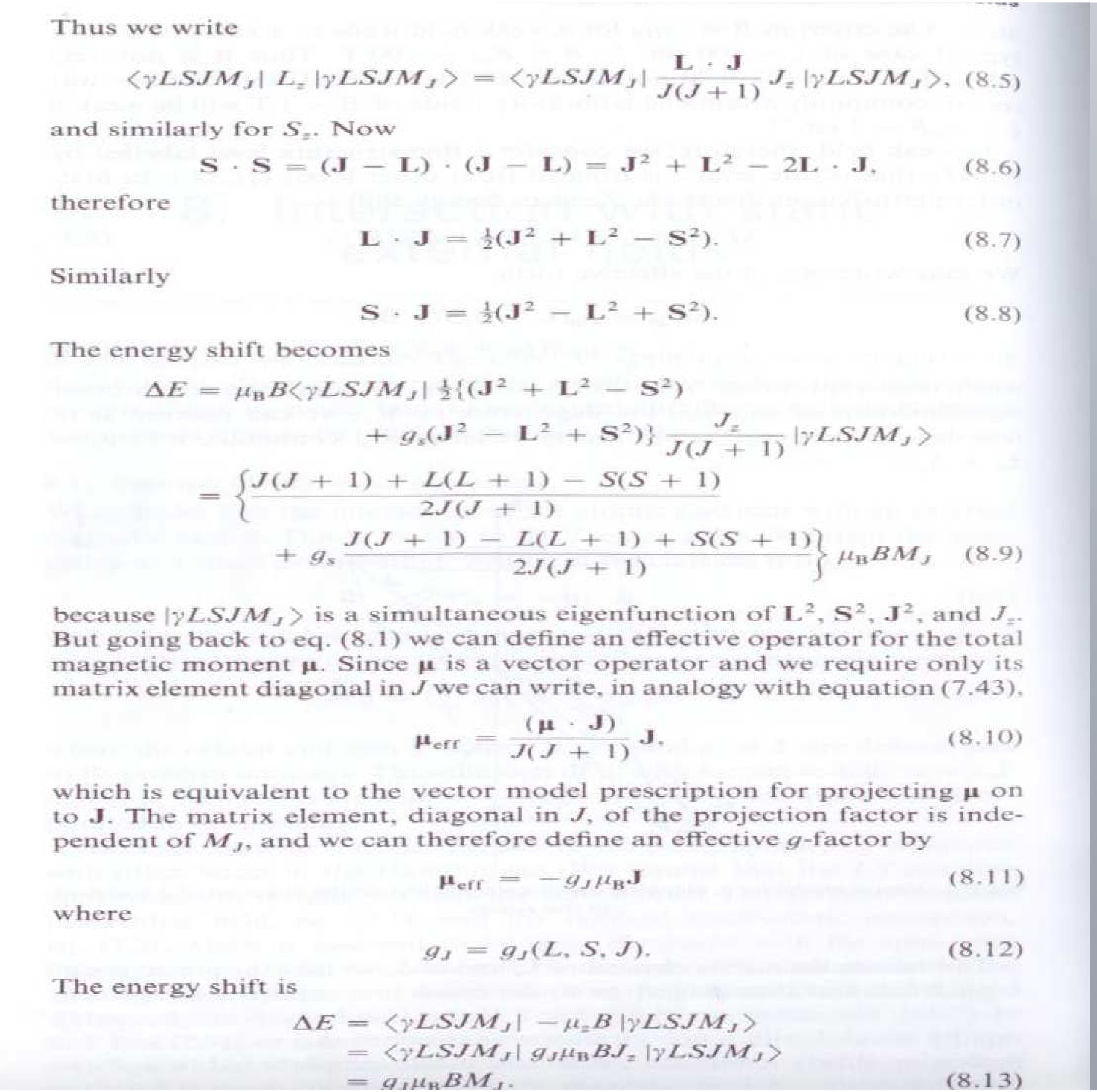
atom. The criterion $B \ll \zeta/\mu_B$ for a weak field leads to a value of B for a typical case of $\zeta \sim 100\ \mathrm{cm}^{-1}$: $B \ll B_{\mathrm{int}} \sim 100\,\mathrm{T}$. Thus it is not very often that the weak-field condition will be violated. Put another way round, commonly attainable laboratory fields of $B \sim 1\ \mathrm{T}$ will be weak if $\zeta \gg \mu_B B \sim 1\ \mathrm{cm}^{-1}$.

In weak field, therefore, we consider a fine-structure level labelled by (γLSJ), that is, the level J is isolated from other levels $(\gamma LSJ')$. In first-order perturbation theory the Zeeman energy shift is

$$\Delta E = \langle \gamma LSJM_J | \mathscr{H}_M | \gamma LSJM_J \rangle. \tag{8.3}$$

We may write $\mathscr{H}_M$ in the effective form

$$\begin{aligned} \mathscr{H}_M &= \mu_B(\mathbf{L} + g_s\mathbf{S}) \cdot \mathbf{B} \\ &= \mu_B B(L_z + g_s S_z). \end{aligned} \tag{8.4}$$



Thus we write

$$\langle \gamma LSJM_J|\, L_z\, |\gamma LSJM_J\rangle = \langle \gamma LSJM_J|\, \frac{\mathbf{L}\cdot\mathbf{J}}{J(J+1)} J_z\, |\gamma LSJM_J\rangle, \tag{8.5}$$

and similarly for S_z. Now

$$\mathbf{S}\cdot\mathbf{S} = (\mathbf{J}-\mathbf{L})\cdot(\mathbf{J}-\mathbf{L}) = \mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{L}\cdot\mathbf{J}, \tag{8.6}$$

therefore

$$\mathbf{L}\cdot\mathbf{J} = \tfrac{1}{2}(\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2). \tag{8.7}$$

Similarly

$$\mathbf{S}\cdot\mathbf{J} = \tfrac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2). \tag{8.8}$$

The energy shift becomes

$$\begin{aligned}\Delta E &= \mu_B B\langle \gamma LSJM_J|\, \tfrac{1}{2}\{(\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2) \\ &\qquad + g_s(\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2)\}\, \frac{J_z}{J(J+1)}\, |\gamma LSJM_J\rangle \\ &= \left\{\frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)}\right. \\ &\qquad \left. + g_s\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}\right\}\mu_B B M_J \end{aligned} \tag{8.9}$$

because $|\gamma LSJM_J\rangle$ is a simultaneous eigenfunction of $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$, and J_z. But going back to eq. (8.1) we can define an effective operator for the total magnetic moment $\boldsymbol{\mu}$. Since $\boldsymbol{\mu}$ is a vector operator and we require only its matrix element diagonal in J we can write, in analogy with equation (7.43),

$$\boldsymbol{\mu}_{\text{eff}} = \frac{(\boldsymbol{\mu}\cdot\mathbf{J})}{J(J+1)}\,\mathbf{J}, \tag{8.10}$$

which is equivalent to the vector model prescription for projecting $\boldsymbol{\mu}$ on to $\mathbf{J}$. The matrix element, diagonal in J, of the projection factor is independent of M_J, and we can therefore define an effective g-factor by

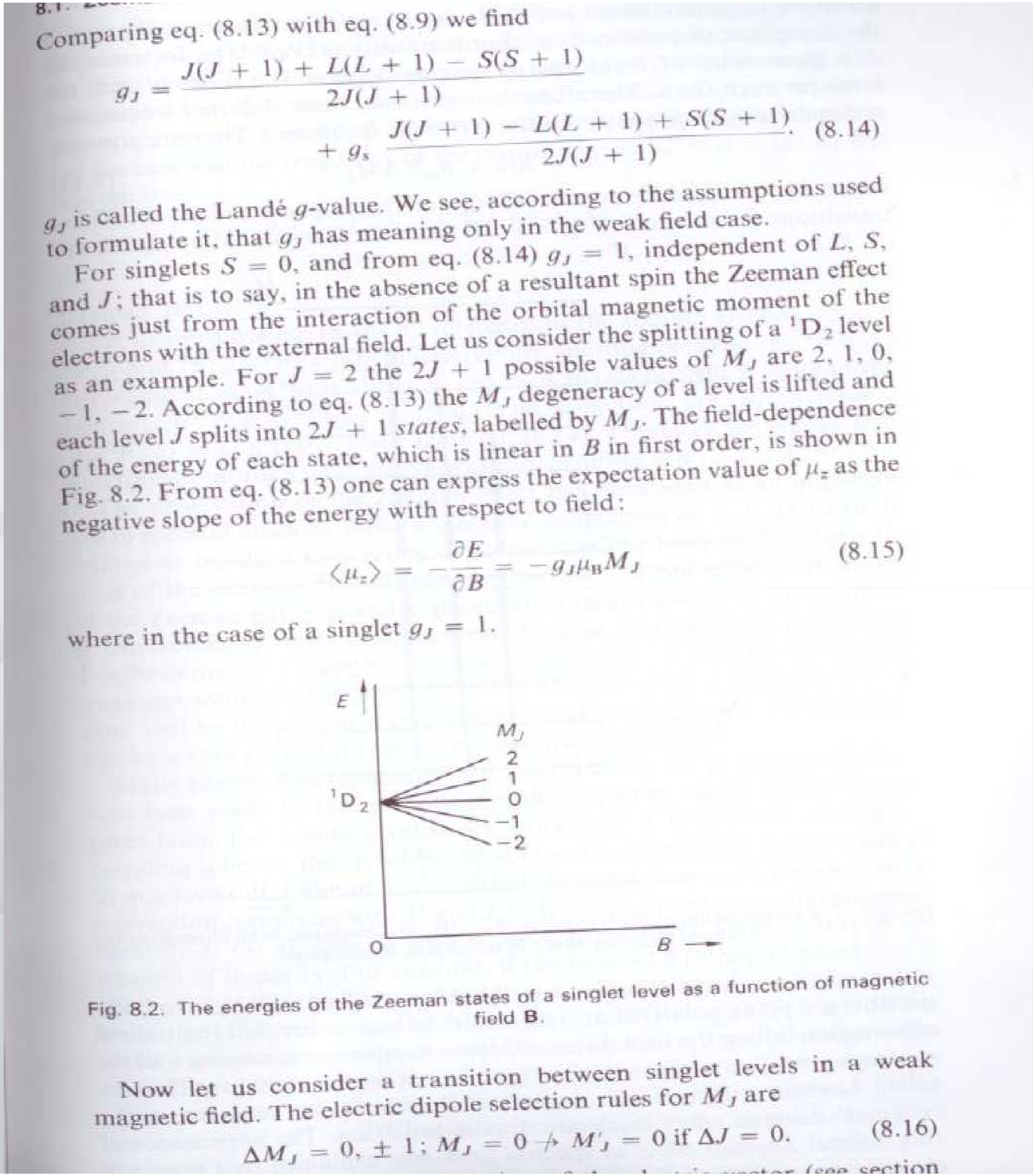
$$\boldsymbol{\mu}_{\text{eff}} = -g_J\mu_B\mathbf{J} \tag{8.11}$$

where

$$g_J = g_J(L, S, J). \tag{8.12}$$

The energy shift is

$$\begin{aligned}\Delta E &= \langle \gamma LSJM_J|\, -\mu_z B\, |\gamma LSJM_J\rangle \\ &= \langle \gamma LSJM_J|\, g_J\mu_B B J_z\, |\gamma LSJM_J\rangle \\ &= g_J\mu_B B M_J. \end{aligned} \tag{8.13}$$



Comparing eq. (8.13) with eq. (8.9) we find

$$g_J = \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} + g_s\,\frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}. \qquad (8.14)$$

g_J is called the Landé g-value. We see, according to the assumptions used to formulate it, that g_J has meaning only in the weak field case.

For singlets $S = 0$, and from eq. (8.14) $g_J = 1$, independent of L, S, and J; that is to say, in the absence of a resultant spin the Zeeman effect comes just from the interaction of the orbital magnetic moment of the electrons with the external field. Let us consider the splitting of a $^1D_2$ level as an example. For $J = 2$ the $2J + 1$ possible values of M_J are 2, 1, 0, −1, −2. According to eq. (8.13) the M_J degeneracy of a level is lifted and each level J splits into $2J + 1$ *states*, labelled by M_J. The field-dependence of the energy of each state, which is linear in B in first order, is shown in Fig. 8.2. From eq. (8.13) one can express the expectation value of μ_z as the negative slope of the energy with respect to field:

$$\langle\mu_z\rangle = -\frac{\partial E}{\partial B} = -g_J\mu_B M_J \qquad (8.15)$$

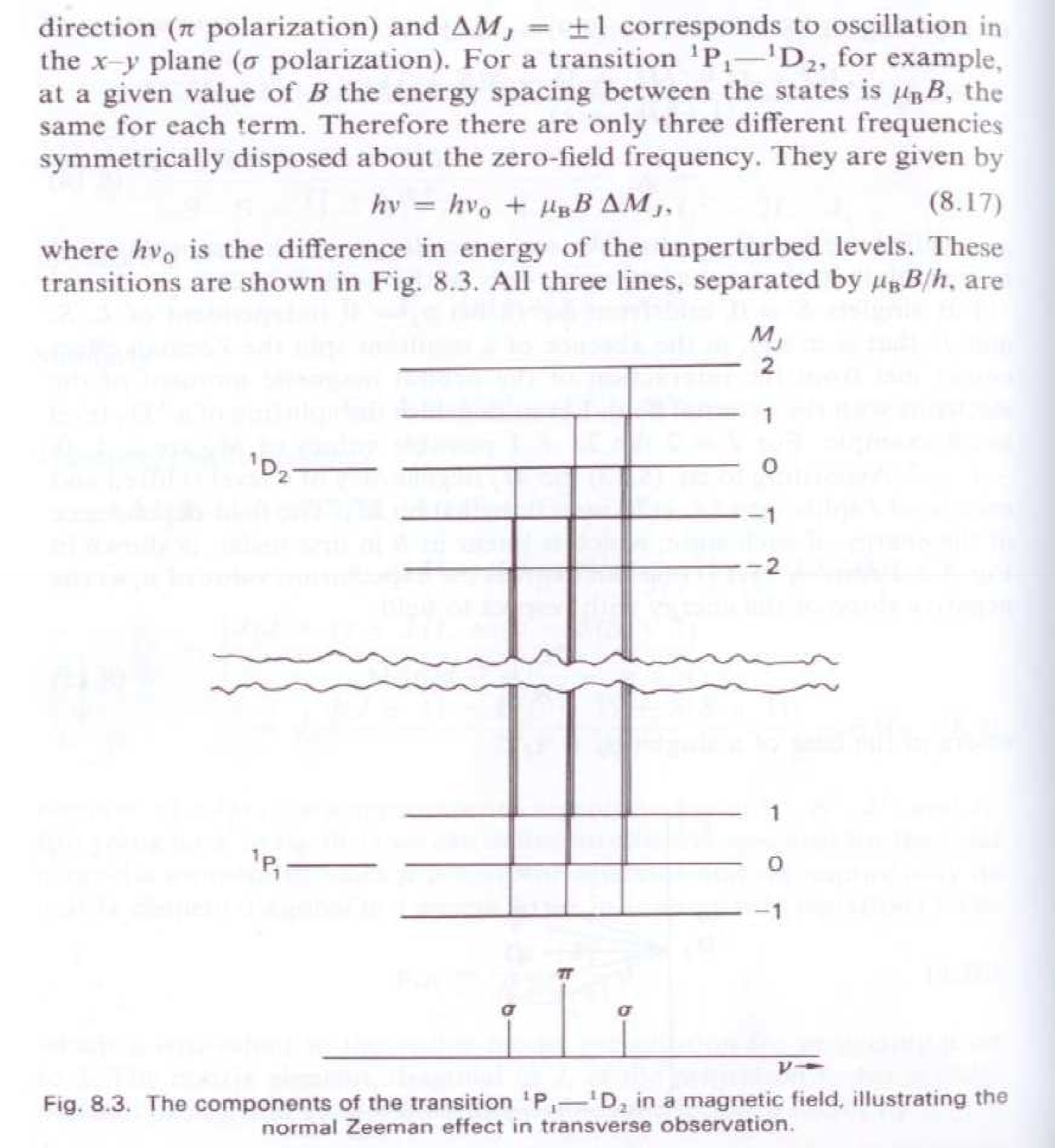
where in the case of a singlet $g_J = 1$.

Fig. 8.2. The energies of the Zeeman states of a singlet level as a function of magnetic field **B**.

Now let us consider a transition between singlet levels in a weak magnetic field. The electric dipole selection rules for M_J are

$$\Delta M_J = 0, \pm 1;\ M_J = 0 \nrightarrow M'_J = 0 \text{ if } \Delta J = 0. \qquad (8.16)$$

Efecto Zeeman normal
Se da en los términos
con S=0
(2S+1=1)



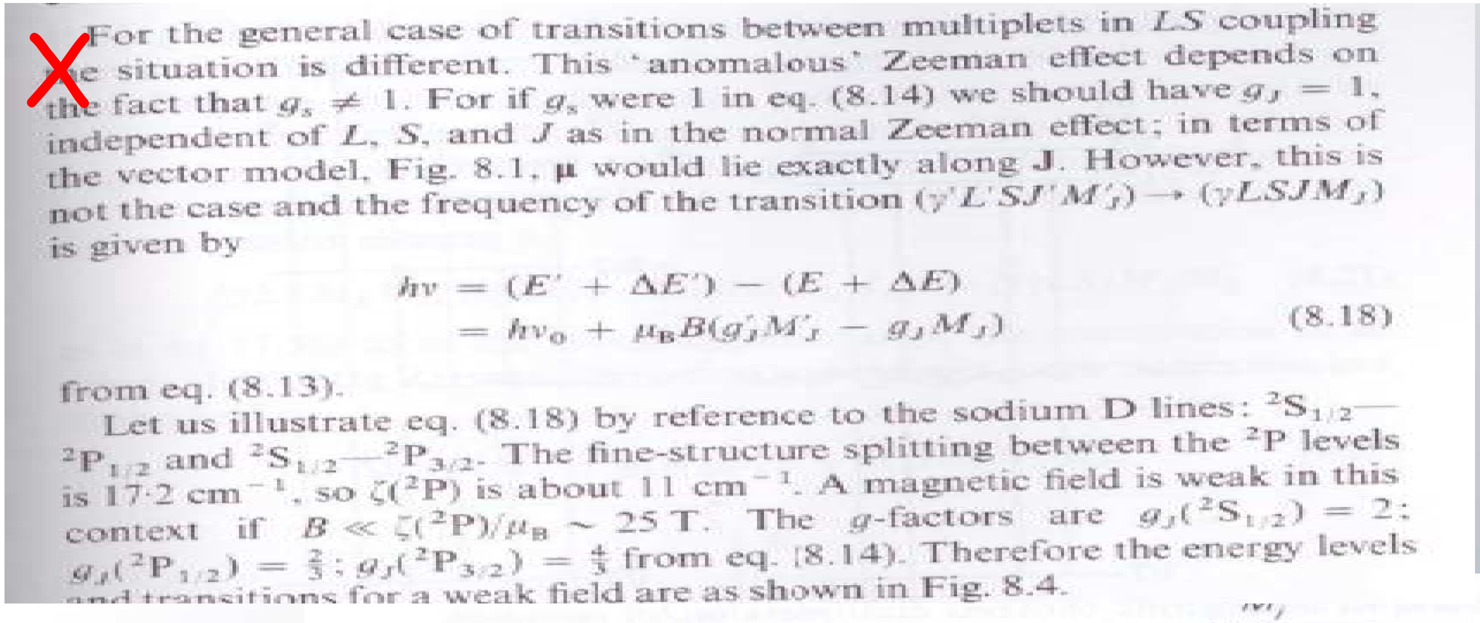
direction (π polarization) and $\Delta M_J = \pm 1$ corresponds to oscillation in the x–y plane (σ polarization). For a transition $^1P_1$—$^1D_2$, for example, at a given value of B the energy spacing between the states is $\mu_B B$, the same for each term. Therefore there are only three different frequencies symmetrically disposed about the zero-field frequency. They are given by

$$h\nu = h\nu_0 + \mu_B B\,\Delta M_J, \tag{8.17}$$

where $h\nu_0$ is the difference in energy of the unperturbed levels. These transitions are shown in Fig. 8.3. All three lines, separated by $\mu_B B/h$, are

Fig. 8.3. The components of the transition $^1P_1$—$^1D_2$ in a magnetic field, illustrating the normal Zeeman effect in transverse observation.

Efecto Zeeman anómalo, para S no nulo



For the general case of transitions between multiplets in LS coupling the situation is different. This 'anomalous' Zeeman effect depends on the fact that $g_s \neq 1$. For if g_s were 1 in eq. (8.14) we should have $g_J = 1$, independent of L, S, and J as in the normal Zeeman effect; in terms of the vector model, Fig. 8.1, $\boldsymbol{\mu}$ would lie exactly along $\mathbf{J}$. However, this is not the case and the frequency of the transition $(\gamma' L' S J' M'_J) \rightarrow (\gamma L S J M_J)$ is given by

$$\begin{aligned} h\nu &= (E' + \Delta E') - (E + \Delta E) \\ &= h\nu_0 + \mu_B B(g'_J M'_J - g_J M_J) \end{aligned} \qquad (8.18)$$

from eq. (8.13).

Let us illustrate eq. (8.18) by reference to the sodium D lines: $^2S_{1/2}$—$^2P_{1/2}$ and $^2S_{1/2}$—$^2P_{3/2}$. The fine-structure splitting between the ^2P levels is 17·2 cm^{-1}, so $\zeta(^2P)$ is about 11 cm^{-1}. A magnetic field is weak in this context if $B \ll \zeta(^2P)/\mu_B \sim 25$ T. The g-factors are $g_J(^2S_{1/2}) = 2$; $g_J(^2P_{1/2}) = \frac{2}{3}$; $g_J(^2P_{3/2}) = \frac{4}{3}$ from eq. (8.14). Therefore the energy levels and transitions for a weak field are as shown in Fig. 8.4.

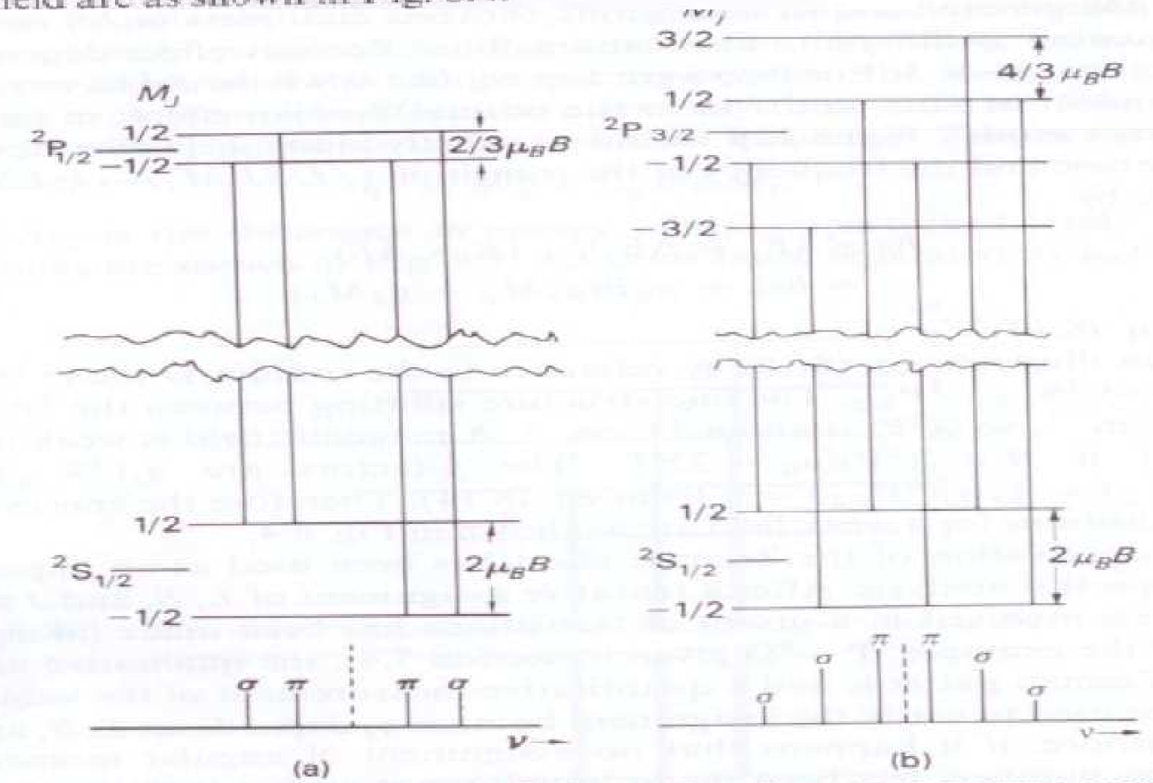
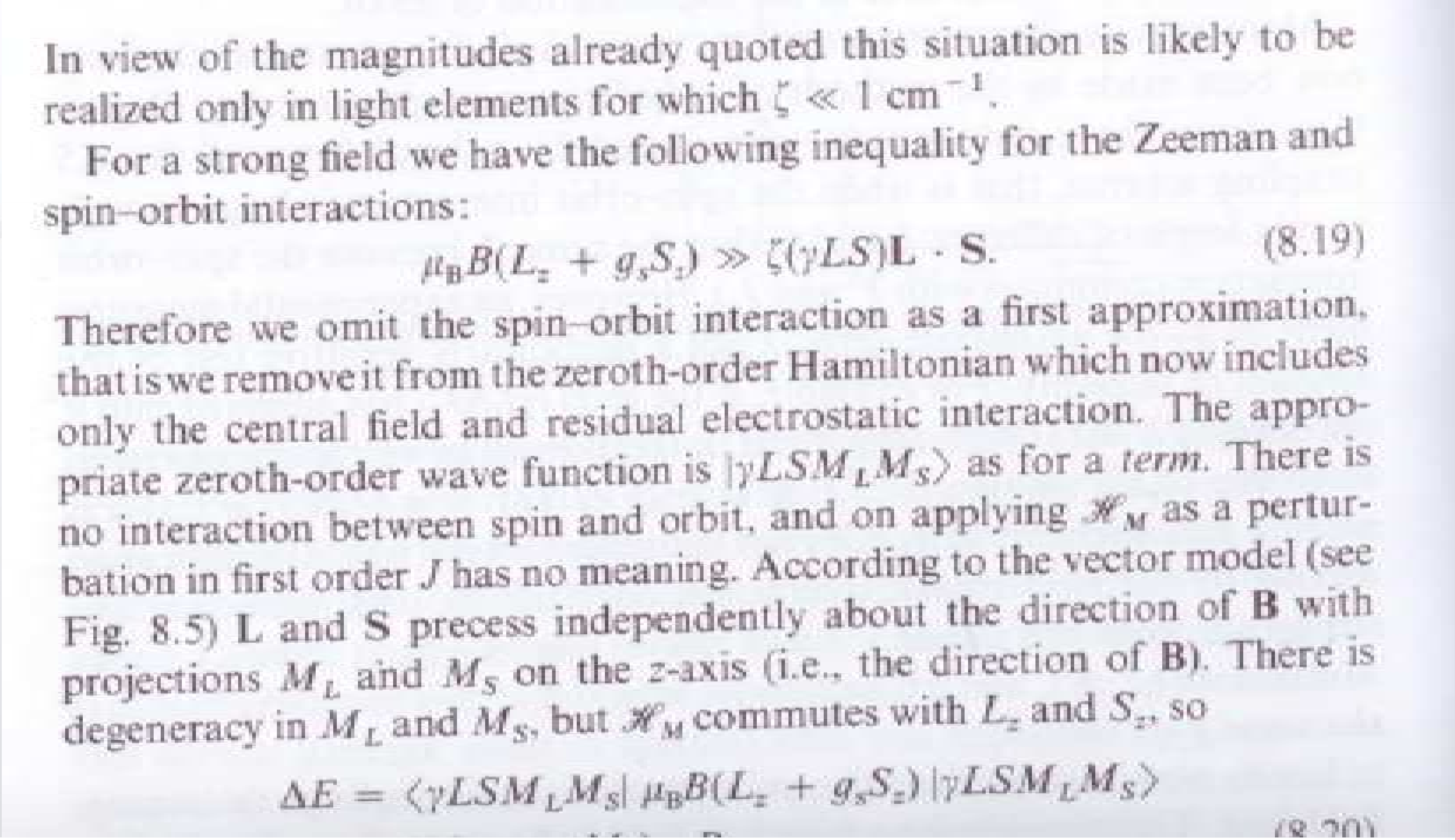


Fig. 8.4. The Zeeman effect in the D lines of sodium, in transverse observation: (a) $^2S_{1/2}$—$^2P_{1/2}$; (b) $^2S_{1/2}$—$^2P_{3/2}$.

Efecto Paschen-Back

Se da cuando el campo magnético es tan grande que el término de interacción con dicho campo es mucho mayor que la interacción de espín-órbita. Como el espín-órbita crece mucho con Z, esta situación de campos 'fuertes' solo se puede dar en átomos ligeros.

En esta situación, el término de espín-órbita se aplica después de considerar el acoplo con el campo magnético, en el esquema $|L, L_z, S, M_s>$



In view of the magnitudes already quoted this situation is likely to be realized only in light elements for which $\zeta \ll 1\ \mathrm{cm}^{-1}$.

For a strong field we have the following inequality for the Zeeman and spin–orbit interactions:

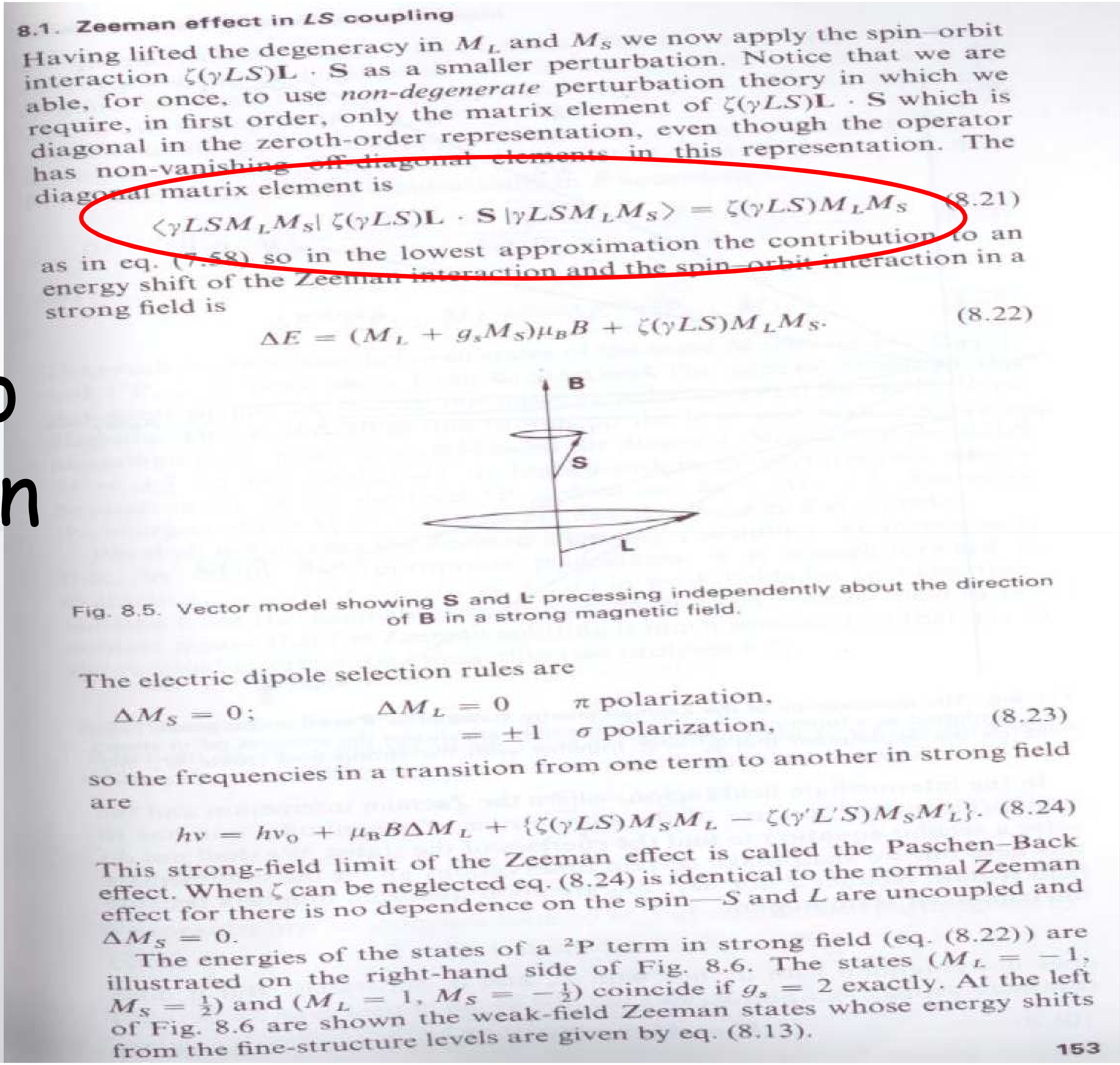
$$\mu_B B(L_z + g_s S_z) \gg \zeta(\gamma LS)\mathbf{L}\cdot\mathbf{S}. \tag{8.19}$$

Therefore we omit the spin–orbit interaction as a first approximation, that is we remove it from the zeroth-order Hamiltonian which now includes only the central field and residual electrostatic interaction. The appropriate zeroth-order wave function is $|\gamma LSM_L M_S\rangle$ as for a *term*. There is no interaction between spin and orbit, and on applying $\mathscr{H}_M$ as a perturbation in first order J has no meaning. According to the vector model (see Fig. 8.5) **L** and **S** precess independently about the direction of **B** with projections M_L and M_S on the z-axis (i.e., the direction of **B**). There is degeneracy in M_L and M_S, but $\mathscr{H}_M$ commutes with L_z and S_z, so

$$\Delta E = \langle \gamma LSM_L M_S | \mu_B B(L_z + g_s S_z) | \gamma LSM_L M_S \rangle$$

(8.20)

Efecto Paschen -Back



8.1. Zeeman effect in *LS* coupling

Having lifted the degeneracy in M_L and M_S we now apply the spin–orbit interaction $\zeta(\gamma LS)\mathbf{L}\cdot\mathbf{S}$ as a smaller perturbation. Notice that we are able, for once, to use *non-degenerate* perturbation theory in which we require, in first order, only the matrix element of $\zeta(\gamma LS)\mathbf{L}\cdot\mathbf{S}$ which is diagonal in the zeroth-order representation, even though the operator has non-vanishing off-diagonal elements in this representation. The diagonal matrix element is

$$\langle\gamma LSM_LM_S|\,\zeta(\gamma LS)\mathbf{L}\cdot\mathbf{S}\,|\gamma LSM_LM_S\rangle = \zeta(\gamma LS)M_LM_S \tag{8.21}$$

as in eq. (7.58) so in the lowest approximation the contribution to an energy shift of the Zeeman interaction and the spin–orbit interaction in a strong field is

$$\Delta E = (M_L + g_sM_S)\mu_BB + \zeta(\gamma LS)M_LM_S. \tag{8.22}$$

Fig. 8.5. Vector model showing **S** and **L** precessing independently about the direction of **B** in a strong magnetic field.

The electric dipole selection rules are

$$\Delta M_S = 0; \qquad \begin{aligned}\Delta M_L &= 0 \quad \pi \text{ polarization,}\\ &= \pm 1 \quad \sigma \text{ polarization,}\end{aligned} \tag{8.23}$$

so the frequencies in a transition from one term to another in strong field are

$$h\nu = h\nu_0 + \mu_BB\Delta M_L + \{\zeta(\gamma LS)M_SM_L - \zeta(\gamma' L'S)M_SM'_L\}. \tag{8.24}$$

This strong-field limit of the Zeeman effect is called the Paschen–Back effect. When ζ can be neglected eq. (8.24) is identical to the normal Zeeman effect for there is no dependence on the spin—S and L are uncoupled and $\Delta M_S = 0$.

The energies of the states of a ^{2}P term in strong field (eq. (8.22)) are illustrated on the right-hand side of Fig. 8.6. The states ($M_L = -1$, $M_S = \frac{1}{2}$) and ($M_L = 1$, $M_S = -\frac{1}{2}$) coincide if $g_s = 2$ exactly. At the left of Fig. 8.6 are shown the weak-field Zeeman states whose energy shifts from the fine-structure levels are given by eq. (8.13).

De Zeeman a Paschen-Back

El campo crece en la figura hacia la derecha. Hay que recordar para completar el diagrama, que los niveles de la misma M_J no se cruzan.

Interaction with static external fields

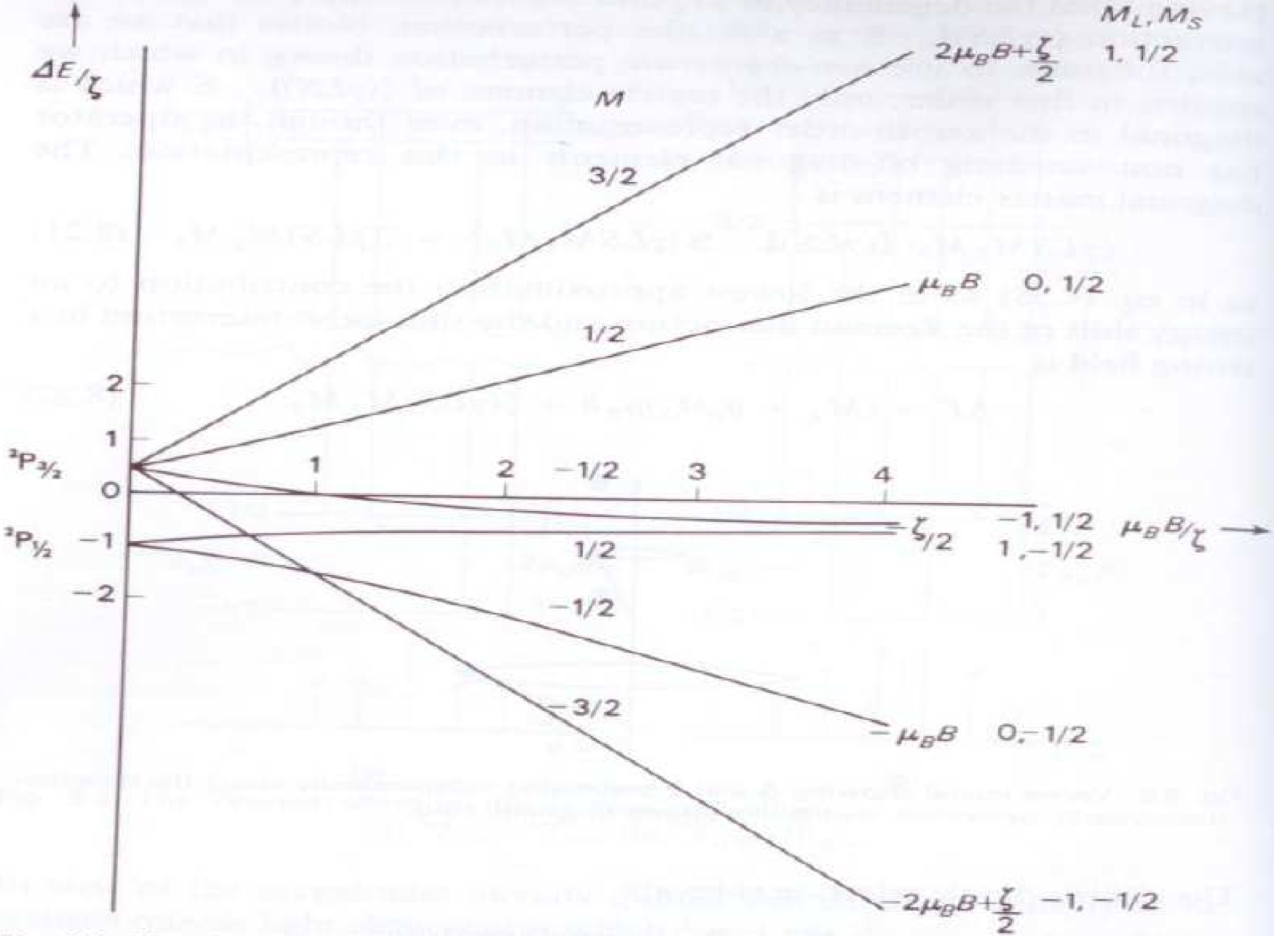


Fig. 8.6. The dependence of the Zeeman energy states of a ^2P term on magnetic field. $\Delta E/\zeta$ is plotted as a function of $\mu_B B/\zeta$. At the right are shown the energies ΔE in strong field, on the assumption that $g_s = 2$, together with the strong-field labels M_L, M_S.

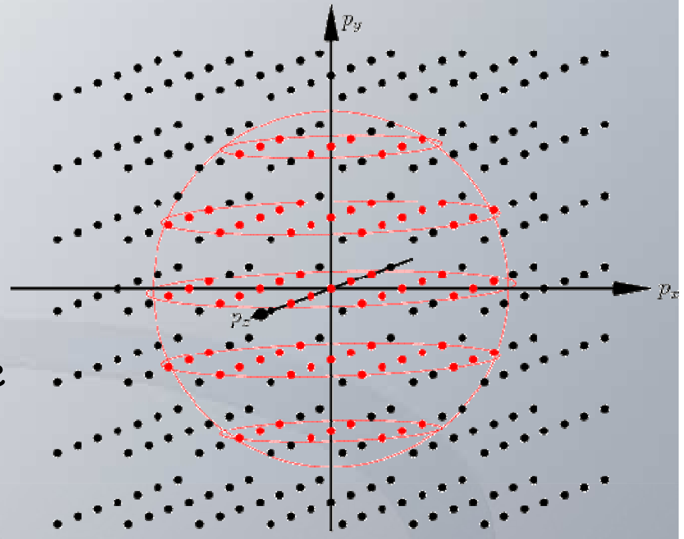
X

Densidad de estados finales

Supongamos un *e (ν)* en una caja finita de anchura L. ¿Cuantos estados permitidos existen con momento *p'<p*?

- Caja finita (L) → Momento cuantizado → $p_i = n_i 2\pi \frac{\hbar}{L}$
- Por lo tanto, el volumen en el espacio de momentos para **cada** valor de $P=(p_x,p_y,p_z)$ vendrá dado por

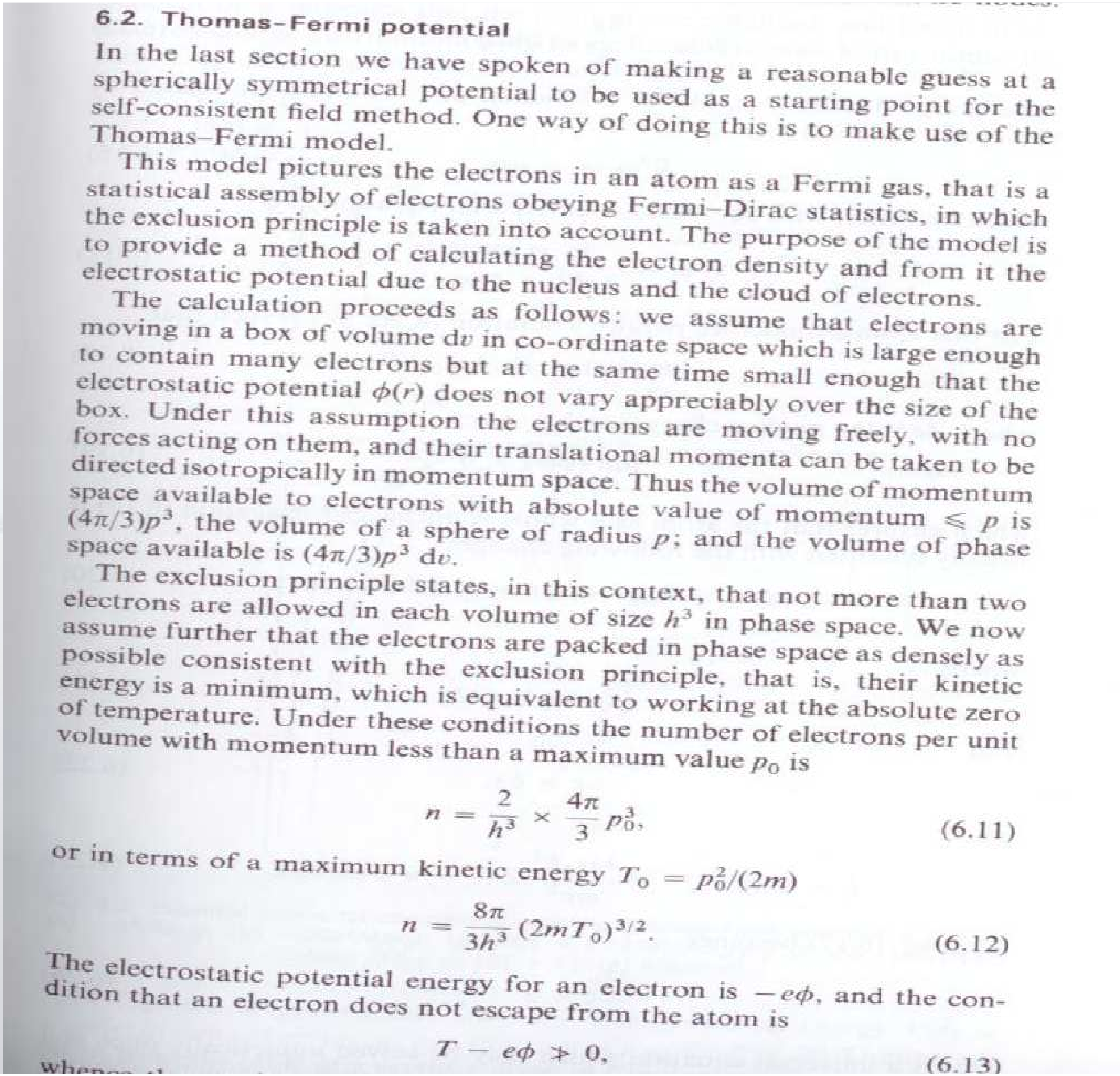
$$Volumen/estado = p_x p_y p_z = \left(2\pi\frac{\hbar}{L}\right)^3 = \frac{(2\pi\hbar)^3}{V}$$



- Los estados con momento *p'<p* serán aquellos que se encuentren dentro de una esfera de radio *p* $\rightarrow \frac{4}{3}\pi p^3$
- Luego el número de *e (ν)* vendrá dado por:

$$n = \frac{\text{Volumen total}}{\text{Volumen /estado}} = \frac{\frac{4}{3}\pi p^3}{\frac{(2\pi\hbar)^3}{V}} = \frac{Vp^3}{6\pi^2\hbar^3} \rightarrow dn = \frac{Vp^2}{2\pi^2\hbar^3}dp$$

En la aproximación de Thomas-Fermi nuclear se toma electrones empaquetados como si ocupasen todos los estados, con la densidad calculada justo arriba, o sea h^3/V



6.2. Thomas–Fermi potential

In the last section we have spoken of making a reasonable guess at a spherically symmetrical potential to be used as a starting point for the self-consistent field method. One way of doing this is to make use of the Thomas–Fermi model.

This model pictures the electrons in an atom as a Fermi gas, that is a statistical assembly of electrons obeying Fermi–Dirac statistics, in which the exclusion principle is taken into account. The purpose of the model is to provide a method of calculating the electron density and from it the electrostatic potential due to the nucleus and the cloud of electrons.

The calculation proceeds as follows: we assume that electrons are moving in a box of volume dv in co-ordinate space which is large enough to contain many electrons but at the same time small enough that the electrostatic potential $\phi(r)$ does not vary appreciably over the size of the box. Under this assumption the electrons are moving freely, with no forces acting on them, and their translational momenta can be taken to be directed isotropically in momentum space. Thus the volume of momentum space available to electrons with absolute value of momentum $\leqslant p$ is $(4\pi/3)p^3$, the volume of a sphere of radius p; and the volume of phase space available is $(4\pi/3)p^3\,dv$.

The exclusion principle states, in this context, that not more than two electrons are allowed in each volume of size h^3 in phase space. We now assume further that the electrons are packed in phase space as densely as possible consistent with the exclusion principle, that is, their kinetic energy is a minimum, which is equivalent to working at the absolute zero of temperature. Under these conditions the number of electrons per unit volume with momentum less than a maximum value p_0 is

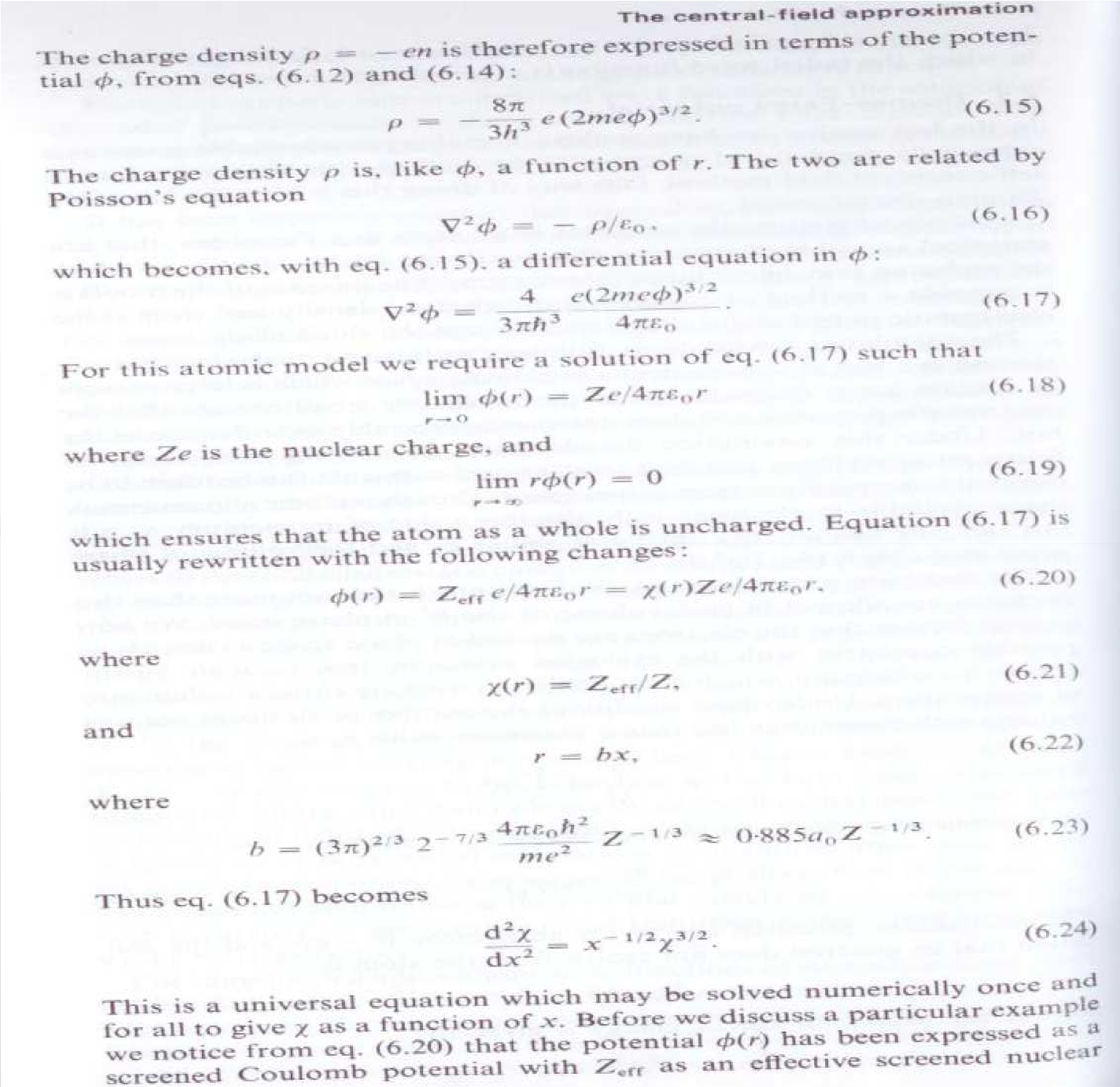
$$n = \frac{2}{h^3} \times \frac{4\pi}{3} p_0^3, \tag{6.11}$$

or in terms of a maximum kinetic energy $T_0 = p_0^2/(2m)$

$$n = \frac{8\pi}{3h^3}(2mT_0)^{3/2}. \tag{6.12}$$

The electrostatic potential energy for an electron is $-e\phi$, and the condition that an electron does not escape from the atom is

$$T - e\phi \ngtr 0, \tag{6.13}$$



The charge density $\rho = -en$ is therefore expressed in terms of the potential ϕ, from eqs. (6.12) and (6.14):

$$\rho = -\frac{8\pi}{3h^3}\, e\,(2me\phi)^{3/2}. \tag{6.15}$$

The charge density ρ is, like ϕ, a function of r. The two are related by Poisson's equation

$$\nabla^2\phi = -\,\rho/\varepsilon_0, \tag{6.16}$$

which becomes, with eq. (6.15), a differential equation in ϕ:

$$\nabla^2\phi = \frac{4}{3\pi h^3}\,\frac{e(2me\phi)^{3/2}}{4\pi\varepsilon_0}. \tag{6.17}$$

For this atomic model we require a solution of eq. (6.17) such that

$$\lim_{r\to 0}\phi(r) = Ze/4\pi\varepsilon_0 r \tag{6.18}$$

where Ze is the nuclear charge, and

$$\lim_{r\to\infty} r\phi(r) = 0 \tag{6.19}$$

which ensures that the atom as a whole is uncharged. Equation (6.17) is usually rewritten with the following changes:

$$\phi(r) = Z_{\text{eff}}\, e/4\pi\varepsilon_0 r = \chi(r) Ze/4\pi\varepsilon_0 r, \tag{6.20}$$

where

$$\chi(r) = Z_{\text{eff}}/Z, \tag{6.21}$$

and

$$r = bx, \tag{6.22}$$

where

$$b = (3\pi)^{2/3}\, 2^{-7/3}\,\frac{4\pi\varepsilon_0 h^2}{me^2}\, Z^{-1/3} \approx 0{\cdot}885 a_0 Z^{-1/3}. \tag{6.23}$$

Thus eq. (6.17) becomes

$$\frac{d^2\chi}{dx^2} = x^{-1/2}\chi^{3/2}. \tag{6.24}$$

This is a universal equation which may be solved numerically once and for all to give χ as a function of x. Before we discuss a particular example we notice from eq. (6.20) that the potential $\phi(r)$ has been expressed as a screened Coulomb potential with Z_{eff} as an effective screened nuclear charge. Also, from eqs. (6.22) and (6.23), we see that b is just a scaling factor for distance from the nucleus: whereas eq. (6.24) which is independent of Z indicates that the form of the potential, and hence of the electron charge distribution, is the same for all Thomas–Fermi atoms, the size of an atom actually decreases slowly as $Z^{-1/3}$.

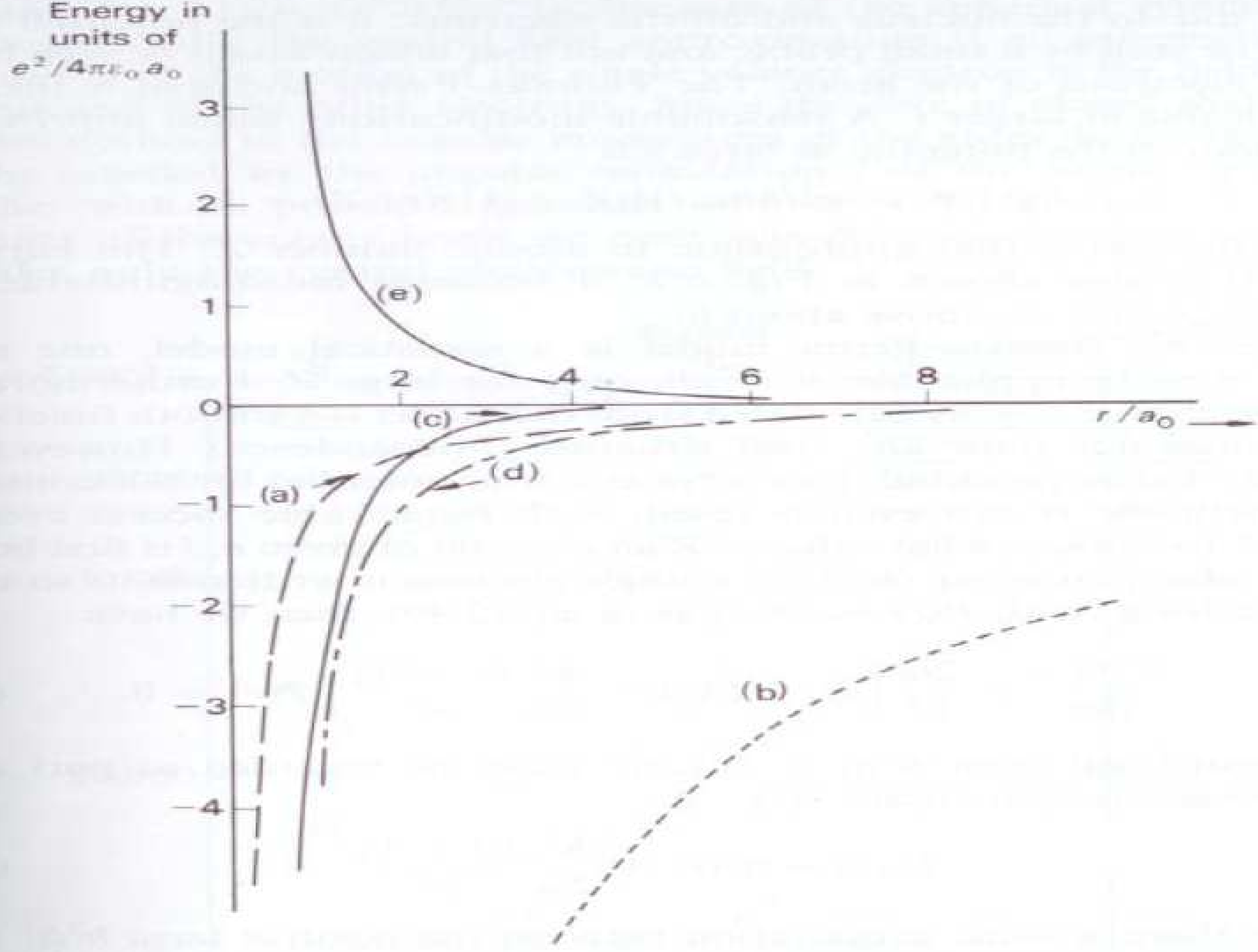


Fig. 6.2. Potential curves for comparison with the Thomas–Fermi potential at $Z = 20$. (a) $-e^2/4\pi\varepsilon_0 r$; (b) $-20e^2/4\pi\varepsilon_0 r$; (c) $V(r) = (-20e^2/4\pi\varepsilon_0 r)\ \chi\ (r;\ 20)$; (d) $(-e^2/4\pi\varepsilon_0 r\ \{19\ \chi\ (r;\ 20) + 1\}$; (e) $h^2 6/2mr^2$.

plotted. The effect of electrostatic screening of the nuclear charge is clearly shown for the Thomas–Fermi potential, which is intermediate between the two extremes ($Z_{\text{eff}} = 1$ and $Z_{\text{eff}} = 20$) in the region $r \sim a_0$. As $r \rightarrow 0$, $V(r) \rightarrow -Ze^2/4\pi\varepsilon_0 r$. But as $r \rightarrow \infty$, $V(r)$ approaches zero much more rapidly than $-e^2/4\pi\varepsilon_0 r$. This behaviour is implicit in one of the assumptions of the model, namely that the Thomas–Fermi potential is that due to the nucleus and *all* the electrons: it is the potential which would be seen by a small probe, and not that which would be seen by one of the electrons of the atom. The Thomas–Fermi potential is therefore inapplicable at larger r. A reasonable modification† which improves the behaviour of the potential at large r is

$$V(r) = (-e^2/4\pi\varepsilon_0 r)\{(Z - 1)\chi(r; Z) + 1\} \qquad (6.25)$$

where the $\chi(r)$ is that appropriate to atomic number Z. This curve for $Z = 20$ is also shown in Fig. 6.2: it becomes indistinguishable from $-e^2/4\pi\varepsilon_0 r$ for r/a_0 above about 6.

Since the Thomas–Fermi model is a statistical model, one might expect it to be applicable, if at all, only for large Z. Furthermore, the electron charge density calculated from the model is a smooth function of r and does not show any shell structure (l-dependence). However, the Thomas–Fermi potential does serve as a trial potential for self-consistent field methods. It can even be used, with remarkable success even for small Z, to show at what value of Z an electron of given n, l is first bound. If the radial part of eq. (6.7) for a single electron is written in its so-called reduced form, with $P(r) = rR(r)$ as in eq. (2.49), then we have

$$\frac{\mathrm{d}^2 P(r)}{\mathrm{d}r^2} + \frac{2m}{\hbar^2}\left(E - U(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)P(r) = 0. \qquad (6.26)$$

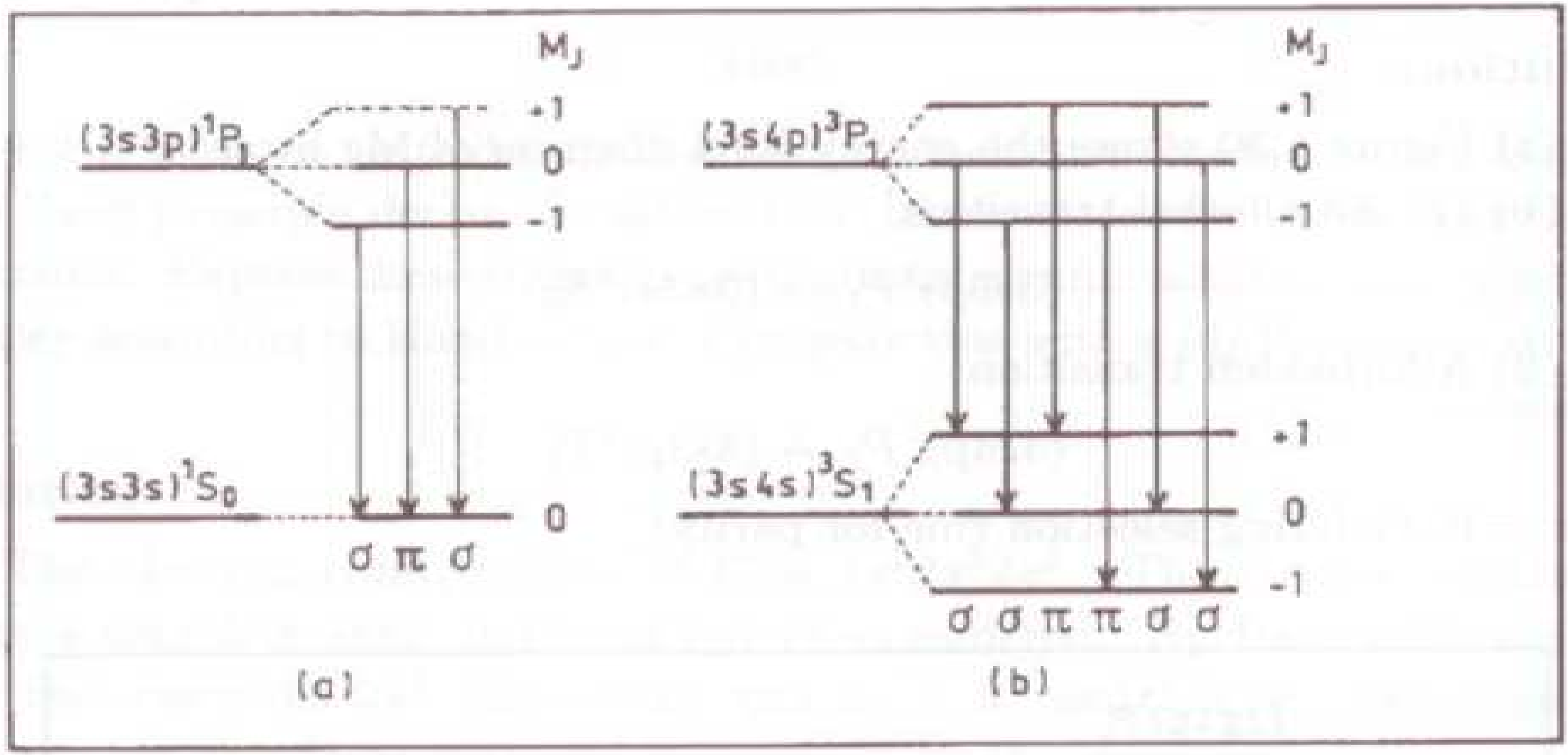
The centrifugal term $\hbar^2 l(l+1)/(2mr^2)$ can be regarded as part of an effective central potential $U'(r)$:

$$U'(r) = U(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}. \qquad (6.27)$$

Clearly there is some cancellation between the positive term $\hbar^2 l(l+1)/(2mr^2)$ and the negative term $U(r)$. An electron of given n, l will not be bound unless $U'(r)$ is negative at some value of r. Bethe‡ indicates the

Algunos problemas

(4) In a magnetic field, the transition $(3s3p)^1P_1 \to (3s3s)^1S_0$ only produces three lines, which is known as normal Zeeman effect, as shown in Fig. 1.31(a). The transition $(3s4p)^3P_1 \to (3s4s)^3S_1$ produces six lines and is known as anomalous Zeeman effect. This is shown in Fig. 1.31(b). The spacings of the sublevels of $(3s3p)^1P_1$, $(3s4p)^3P_1$, and $(3s4s)^3S_1$ are $\mu_B B$, $3\mu_B B/2$ and $2\mu_B B$ respectively.



What is meant by the statement that the ground state of the carbon atom has the configuration $(1s)^2(2s)^2(2p)^2$?

Assuming that Russell-Saunders coupling applies, show that there are 5 spectroscopic states corresponding to this configuration: ${}^1S_0$, ${}^1D_2$, ${}^3P_1$, ${}^3P_2$, ${}^3P_0$.

Solution:

The electronic configuration of the ground state of carbon being $(1s)^2$ $(2s)^2(2p)^2$ means that, when the energy of carbon atom is lowest, there are two electrons on the s-orbit of the first principal shell and two electrons each on the s- and p-orbits of the second principal shell.

The spectroscopic notations corresponding to the above electronic configuration are determined by the two equivalent electrons on the p-orbit.

For these two p-electrons, the possible combinations and sums of the values of the z-component of the orbital quantum number are as follows:

m_{l2}	m_{l1}	1	0	-1
1		2	1	0
0		1	0	-1
-1		0	-1	-2

For $m_{l1} = m_{l2}$, or $L = 2, 0$, Pauli's principle requires $m_{s1} \neq m_{s2}$, or $S = 0$, giving rise to terms ${}^1D_2$, ${}^1S_0$.

For $m_{s1} = m_{s2}$, or $S = 1$, Pauli's principle requires $m_{l1} \neq m_{l2}$, or $L = 1$, and so $J = 2,1,0$, giving rise to terms ${}^3P_{2,1,0}$. Hence corresponding to the electron configuration $1s^22s^22p^2$ the possible spectroscopic terms are

Apply the Russell-Saunders coupling scheme to obtain all the states associated with the electron configuration $(1s)^2(2s)^2(2p)^5(3p)$. Label each state by the spectroscopic notation of the angular-momentum quantum numbers appropriate to the Russell-Saunders coupling.

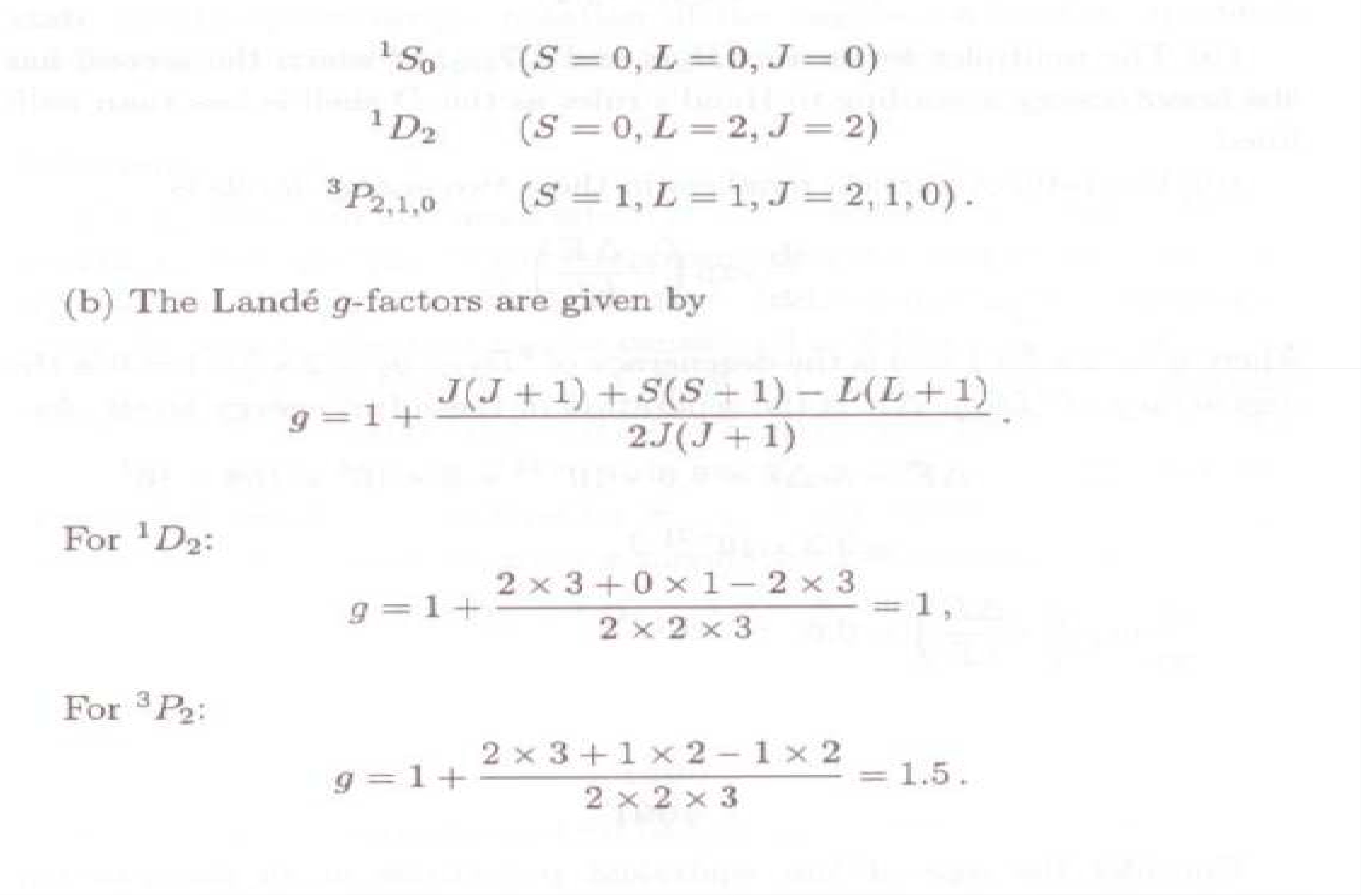
NOTA: la configuracion p^n y la p^{6-n} son equivalentes, Así para estudiar 5 electrones en la capa p, vale estudiar el caso de un electrón en la capa p. Lo mismo para otras capas. Es similar a lo que veíamos con los núcleos: agujero en capa=nucleón soltero

Solution:

The 2*p*-orbit can accommodate $2(2l+1)=6$ electrons. Hence the configuration $(1s)^2(2s)^2(2p)^5$ can be represented by its complement $(1s)^2(2s)^2(2p)^1$ in its coupling with the 3*p* electron. In LS coupling the combination of the 2*p*- and 3*p*-electrons can be considered as follows. As $l_1=1$, $l_2=1$, $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$, we have $L=2,1,0$; $S=1,0$. For $L=2$, we have for $S=1$: $J=3,2,1$; and for $S=0$: $J=2$, giving rise to ${}^3D_{3,2,1}$, ${}^1D_2$. For $L=1$, we have for $S=1$: $J=2,1,0$; and for $S=0$: $J=1$, giving rise to ${}^3P_{2,1,0}$, ${}^1P_1$. For $L=0$, we have for $S=1$: $J=1$; for $S=0$: $J=0$, giving rise to ${}^3S_1$, ${}^1S_0$. Hence the given configuration has atomic states

$$ {}^3S_1, {}^3P_{2,1,0}, {}^3D_{3,2,1}, {}^1S_0, {}^1P_1, {}^1D_2 . $$

Si tenemos en cuenta el principio de exclusión de Pauli, nos quedan los términos:



$$
\begin{aligned}
&{}^1S_0 \qquad (S=0, L=0, J=0)\\
&{}^1D_2 \qquad (S=0, L=2, J=2)\\
&{}^3P_{2,1,0} \qquad (S=1, L=1, J=2,1,0)\,.
\end{aligned}
$$

(b) The Landé g-factors are given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\,.$$

For ${}^1D_2$:

$$g = 1 + \frac{2\times 3 + 0\times 1 - 2\times 3}{2\times 2\times 3} = 1\,,$$

For ${}^3P_2$:

$$g = 1 + \frac{2\times 3 + 1\times 2 - 1\times 2}{2\times 2\times 3} = 1.5\,.$$

(a) What is the electron configuration of sodium ($Z = 11$) in its ground state? In its first excited state?

(b) Give the spectroscopic term designation (e.g. ${}^4S_{3/2}$) for each of these states in the LS coupling approximation.

(c) The transition between the two states is in the visible region. What does this say about kR, where k is the wave number of the radiation and R is the radius of the atom? What can you conclude about the multipolarity of the emitted radiation?

(d) What are the sodium "*D*-lines" and why do they form a doublet?

Solution:

(a) The electron configuration of the ground state of Na is $1s^22s^22p^63s^1$, and that of the first excited state is $1s^22s^22p^63p^1$.

(b) The ground state: ${}^2S_{1/2}$.

The first excited state: ${}^2P_{3/2}, {}^2P_{1/2}$.

(c) As the atomic radius $R \approx 1$ Å and for visible light $k \approx 10^{-4}$ Å^{-1}, we have $kR \ll 1$, which satisfies the condition for electric-dipole transition. Hence the transitions ${}^2P_{3/2} \to {}^2S_{1/2}$, ${}^2P_{1/2} \to {}^2S_{1/2}$ are electric dipole transitions.

(d) The *D*-lines are caused by transition from the first excited state to the ground state of Na. The first excited state is split into two energy levels ${}^2P_{3/2}$ and ${}^2P_{1/2}$ due to LS coupling. Hence the *D*-line has a doublet structure.

Couple a p-state and an s-state electron via

(a) Russell-Saunders coupling,

(b) j, j coupling,

and identify the resultant states with the appropriate quantum numbers. Sketch side by side the energy level diagrams for the two cases and show which level goes over to which as the spin-orbit coupling is increased.

We have $s_1 = s_2 = 1/2$, $l_1 = 1$, $l_2 = 0$.

(a) In LS coupling, $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$, $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Thus $L = 1, S = 1, 0$.

For $S = 1, J = 2, 1, 0$, giving rise to ${}^3P_{2,1,0}$.

For $S = 0, J = 1$, giving rise to ${}^1P_1$.

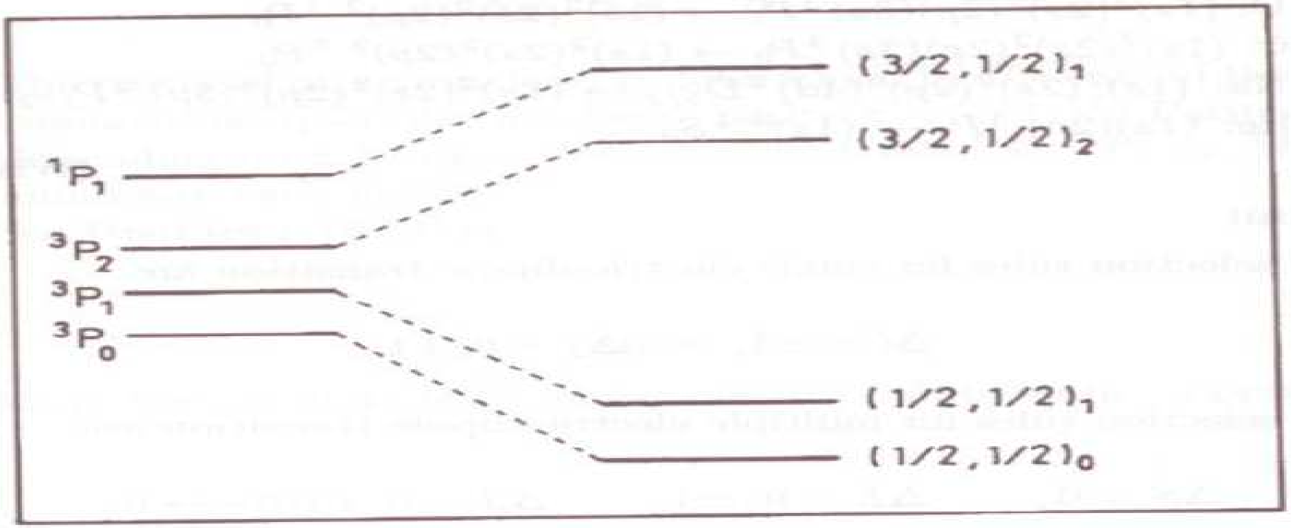
(b) In jj coupling, $\mathbf{j}_1 = \mathbf{l}_1 + \mathbf{s}_1$, $\mathbf{j}_2 = \mathbf{l}_2 + \mathbf{s}_2$, $\mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$. Thus $j_1 = \frac{3}{2}, \frac{1}{2}$, $j_2 = \frac{1}{2}$.

Hence the coupled states are

$$\left(\frac{3}{2}, \frac{1}{2}\right)_2, \left(\frac{3}{2}, \frac{1}{2}\right)_1, \left(\frac{1}{2}, \frac{1}{2}\right)_1, \left(\frac{1}{2}, \frac{1}{2}\right)_0,$$

where the subscripts indicate the values of J.

The coupled states are shown in



For each of the following atomic radiative transitions, indicate whether the transition is allowed or forbidden under the electric-dipole radiation selection rules. For the forbidden transitions, cite the selection rules which are violated.

(a) He: $(1s)(1p)\ {}^1P_1 \rightarrow (1s)^2\ {}^1S_0$
(b) C: $(1s)^2(2s)^2(2p)(3s)\ {}^3P_1 \rightarrow (1s)^2(2s)^2(2p)^2\ {}^3P_0$
(c) C: $(1s)^2(2s)^2(2p)(3s)\ {}^3P_0 \rightarrow (1s)^2(2s)^2(2p)^2\ {}^3P_0$
(d) Na: $(1s)^2(2s)^2(2p)^6(4d)\ {}^2D_{5/2} \rightarrow (1s)^2(2s)^2(2p)^6(3p)\ {}^2P_{1/2}$
(e) He: $(1s)(2p)\ {}^3P_1 \rightarrow (1s)^2\ {}^1S_0$

Solution:

The selection rules for single electric-dipole transition are

$$\Delta l = \pm 1, \qquad \Delta j = 0, \pm 1 .$$

The selection rules for multiple electric-dipole transition are

$$\Delta S = 0\,, \qquad \Delta L = 0\,, \pm 1, \qquad \Delta J = 0, \pm 1 (0 \not\leftrightarrow 0) .$$

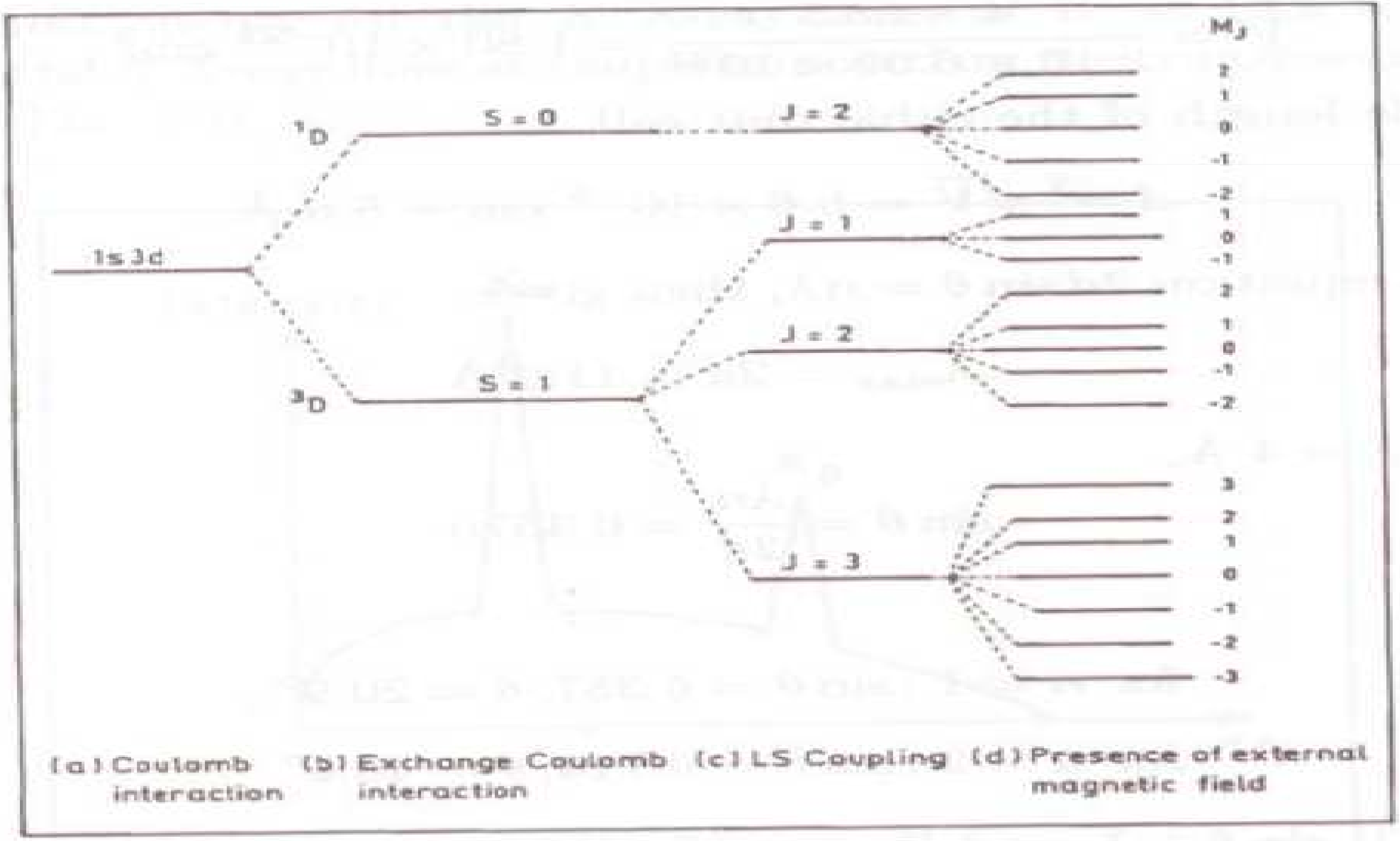
(a) Allowed electric-dipole transition.
(b) Allowed electric-dipole transition.
(c) Forbidden as the total angular momentum J changes from 0 to 0 which is forbidden for electric-dipole transition.
(d) Forbidden as it violates the condition $\Delta J = 0, \pm 1$.
(e) Forbidden as it violates the condition $\Delta S = 0$.

Consider a helium atom with a $1s3d$ electronic configuration. Sketch a series of energy-level diagrams to be expected when one takes successively into account:

(a) only the Coulomb attraction between each electron and the nucleus,
(b) the electrostatic repulsion between the electrons,
(c) spin-orbit coupling,
(d) the effect of a weak external magnetic field.

Solution:

The successive energy-level splittings are shown :



The atomic number of aluminum is 13.

(a) What is the electronic configuration of Al in its ground state?

(b) What is the term classification of the ground state? Use standard spectroscopic notation (e.g. $^4S_{1/2}$) and explain all superscripts and subscripts.

(c) Show by means of an energy-level diagram what happens to the ground state when a very strong magnetic field (Paschen-Back region) is applied. Label all states with the appropriate quantum numbers and indicate the relative spacing of the energy levels.

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1 .$$

(b) The spectroscopic notation of the ground state of Al is $^2P_{1/2}$, where the superscript 2 is the multiplet number, equal to $2S+1$, S being the total spin quantum number, the subscript 1/2 is the total angular momentum quantum number, the letter P indicates that the total orbital angular momentum quantum number $L=1$.

(c) In a very strong magnetic field, LS coupling will be destroyed, and the spin and orbital magnetic moments interact separately with the external magnetic field, causing the energy level to split. The energy correction in the magnetic field is given by

$$\Delta E = -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_s)\cdot \mathbf{B} = (M_L + 2M_s)\mu_B B ,$$

where

$$M_L = 1, 0, -1, \qquad M_S = 1/2, -1/2 .$$

The ^2P energy level is separated into 5 levels, the spacing of neighboring levels being $\mu_B B$. The split levels and the quantum numbers (L, S, M_L, M_S) are shown in Fig. 1.53.