Atomic Structure and Spectra

本章節將探討如何用量子力學來描述原子的電子結構，電子是如何在原子核周圍運轉。

名詞: hydrogenic atoms(or called hydrogen like atoms),H , He^{+} , Li^{2+} ,U^{91+}, spectroscopy , spectrum(spectra) , spectrometer , spectrometry , wavenumber(1/λ)

氫原子光譜

Lyman series (*n*=1), Balmer series (*n*=2) , Paschen series (*n*=3)

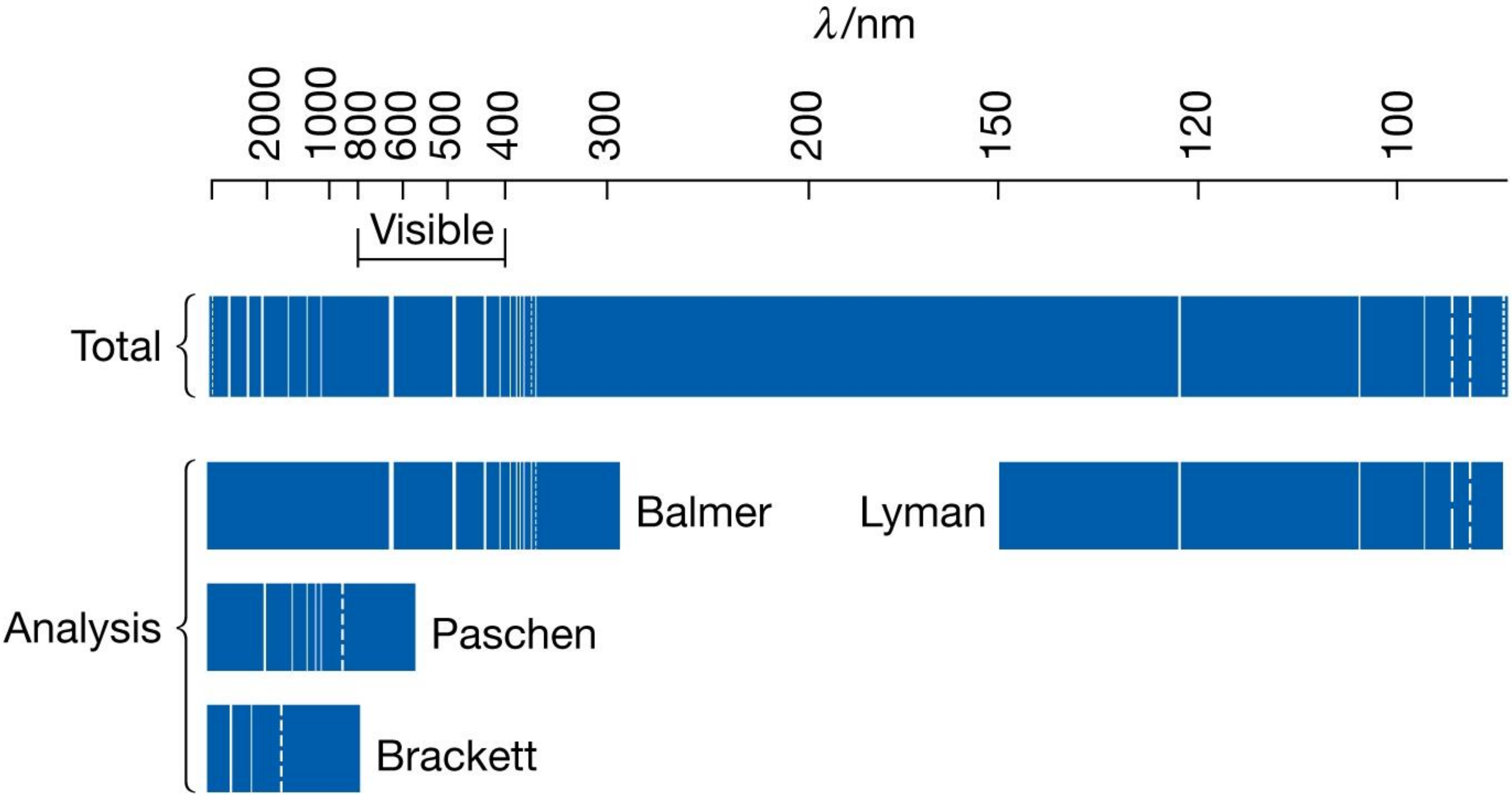
$$\tilde{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right) \qquad R_{\mathrm{H}} = 109677 cm^{-1} (Rydberg\ const) \quad n_2 > n_1$$

$Ritz\ combination\ principle:$

以 $spectroscopic\ \ terms,\ T_1 = \frac{R_H}{n_1^2},\ \frac{R_H}{n_2^2} = T_2$,來表示光譜之形式,如上式

$\tilde{\nu} = T_1 - T_2$,適用於所有原子或分子光譜的形式

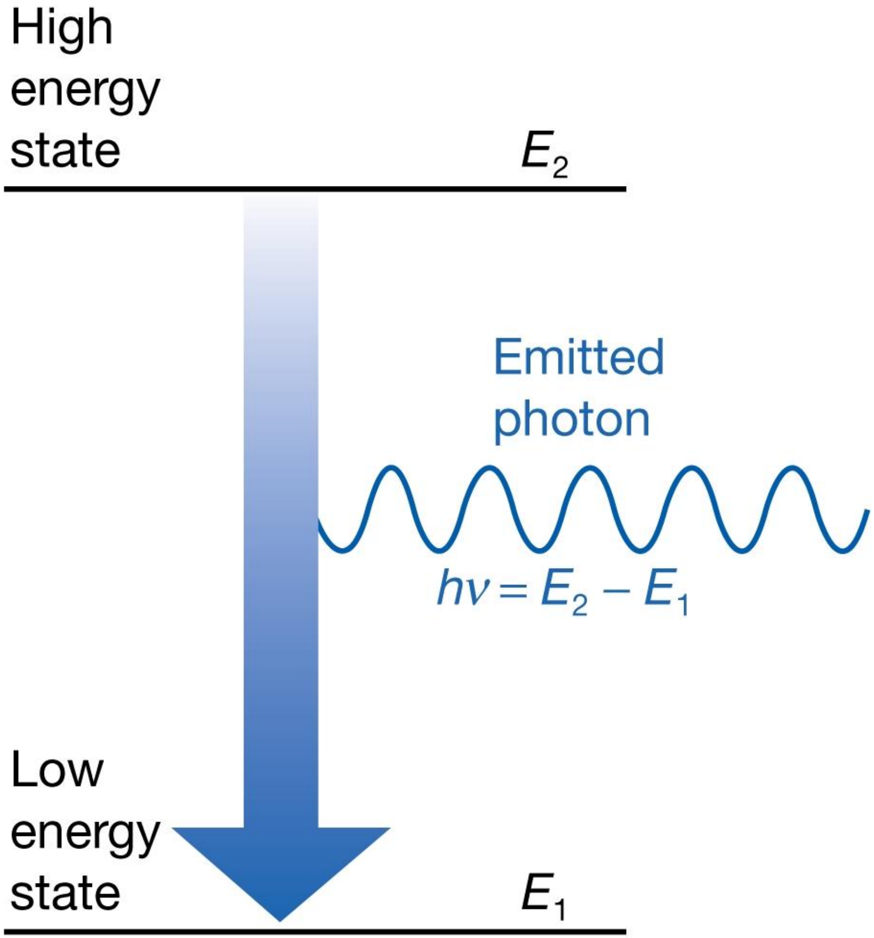
,然而只有$hydrogenic\ atom$,其$T = \frac{const}{n^2}$得簡單形式


λ/nm
2000
1000
800
600
500
400
300
200
150
120
100
Visible
Total
Analysis
Balmer
Lyman
Paschen
Brackett

Bohr frequency condition:

when an atom changes its energy by $\Delta E = h\nu = hcT_1 - hcT_2 \quad \therefore \nu = cT_1 - cT_2$

所得光譜現象要如何用量子力學來解釋?



Schrödinger equation $\hat{\mathrm{H}}\Psi = E\Psi$

其中 $\hat{\mathrm{H}} = ?$ 動能 (電子動能, $-\dfrac{\hbar^2}{2m_e}\nabla_e^2\Psi$; 核動能, $-\dfrac{\hbar^2}{2m_N}\nabla_N^2\Psi$)

位能 (電子與核間位能; $\mathrm{V} = -\dfrac{Ze^2}{4\pi\varepsilon_\circ r}$)

方法:先將電子與核的相對運動與整個原子的運動分開(觀察著站在原子上);然後再將電子與核的相對運動的三個 coordinates 分離成 angular part 和 radial part .其中 angular part 已在前章講過(3-D rotation), ℓ, m_ℓ 兩個 quantum number,而 radial part, 有一 quantum number, n ,起源於電子與核的 boundary condition.

電子與核的相對運動,寫成$Schr\ddot{o}dinger\; equation$

$-\frac{\hbar^2}{2\mu}\nabla^2\Psi+V\Psi=E\Psi$,其中$\frac{1}{\mu}=\frac{1}{m_e}+\frac{1}{m_N}$,該 μ與m_e很接近 , 除非做非常精確的計算,一般就用 m_e代之

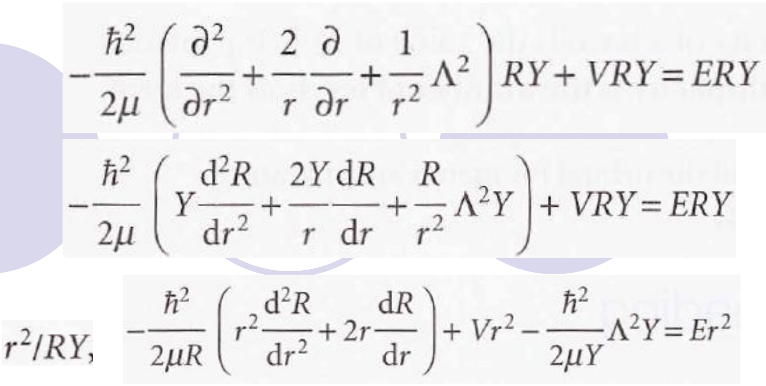
$\Psi(r,\theta,\phi)=R(r)\,Y(\theta,\phi)$ 為電子與核的相對運動 $wavef_N$

$$\nabla^2=\underset{\text{與}R(r)\text{有關}}{\underline{\underline{\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}}}}+\frac{1}{r^2}\underset{\text{與}Y(\theta,\phi)\text{有關}}{\underline{\underline{\Lambda^2}}},\qquad V=-\frac{Z\,e^2}{4\pi\,\varepsilon_\circ r}$$

$$\therefore\nabla^2\,\Psi(r,\theta,\phi)=\nabla^2R(r)\,Y(\theta,\phi)$$

$$=\left(\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{dr}\right)\big(Y(\theta,\phi)\big)+\left(\frac{1}{r^2}\Lambda^2\,Y\big(\theta,\phi\big)\right)(R(r))$$

$$=\left(\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{dr}\right)\big(Y(\theta,\phi)\big)+\frac{1}{r^2}\ell(\ell+1)Y\big(\theta,\phi\big)(R(r))$$



$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2\right)RY+VRY=ERY$$

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+\frac{2Y}{r}\frac{\mathrm{d}R}{\mathrm{d}r}+\frac{R}{r^2}\Lambda^2Y\right)+VRY=ERY$$

r^2/RY, $$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2r\frac{\mathrm{d}R}{\mathrm{d}r}\right)+Vr^2-\frac{\hbar^2}{2\mu Y}\Lambda^2Y=Er^2$$

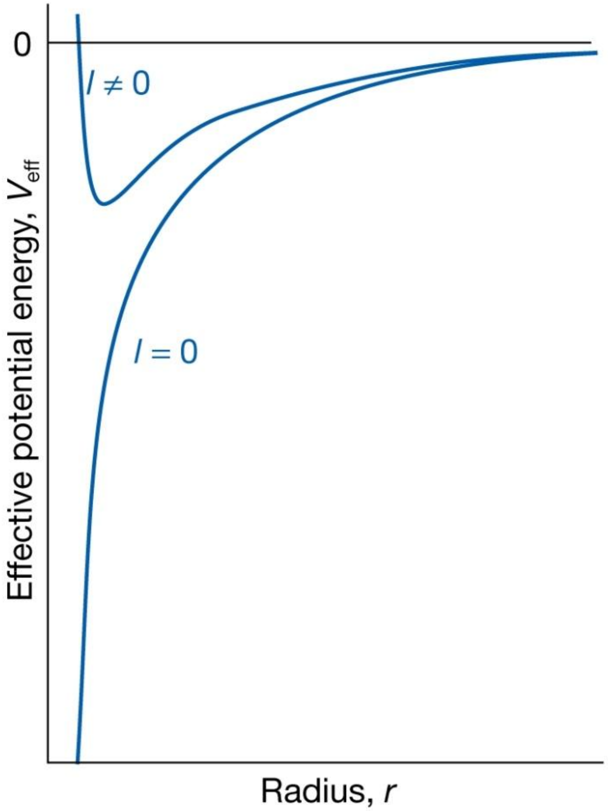
代入 $-\frac{\hbar^2}{2\mu}\nabla^2\psi+V\psi=E\psi$ 中

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R(r)}{d\,r^2}+\frac{2}{r}\frac{dR(r)}{d\,r}\right)Y(\theta,\phi)+\frac{\ell(\ell+1)\hbar^2}{2\,\mu r^2}R(r)Y(\theta,\phi)-\frac{Ze^2}{4\pi\varepsilon_0 r}R(r)Y(\theta,\phi)$$
$$=E\,R(r)Y(\theta,\phi)$$

除以 $Y(\theta,\phi)$, $\therefore -\frac{\hbar^2}{2\mu}\left(\frac{d^2R(r)}{d\,r^2}+\frac{2}{r}\frac{dR(r)}{d\,r}\right)+\left(-\frac{Z\,e^2}{4\,\pi\,\varepsilon_0 r}+\frac{\ell(\ell+1)\hbar^2}{2\,\mu r^2}\right)R(r)=E\,R(r)$

$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R(r)}{d\,r^2}+\frac{2}{r}\frac{dR(r)}{d\,r}\right)+V_{eff}R(r)=ER(r)$ → *schrödingerequation for radial part*

其中 R(r)表示電子距核為 r，在此一度空間上 motion 所展示出的 wavefN，而 V_{eff} 代表電子與核的靜電位能及電子繞核做三度空間旋轉的動能, $\frac{L^2}{2I}$ 。



經解微分方程，得 $R(r)=R_{n,\ell}(r)=N_{n,\ell}\ (\rho)^{\ell}\ L_{n,\ell}(\rho)\ e^{(-\frac{\rho}{2})}$

而 $L_{n,\ell}(\rho)$ 稱為 associated Laguerre polynomial (受控於二個 quantum number, n,ℓ 皆為正整數，但 $\ell < n$)。其中

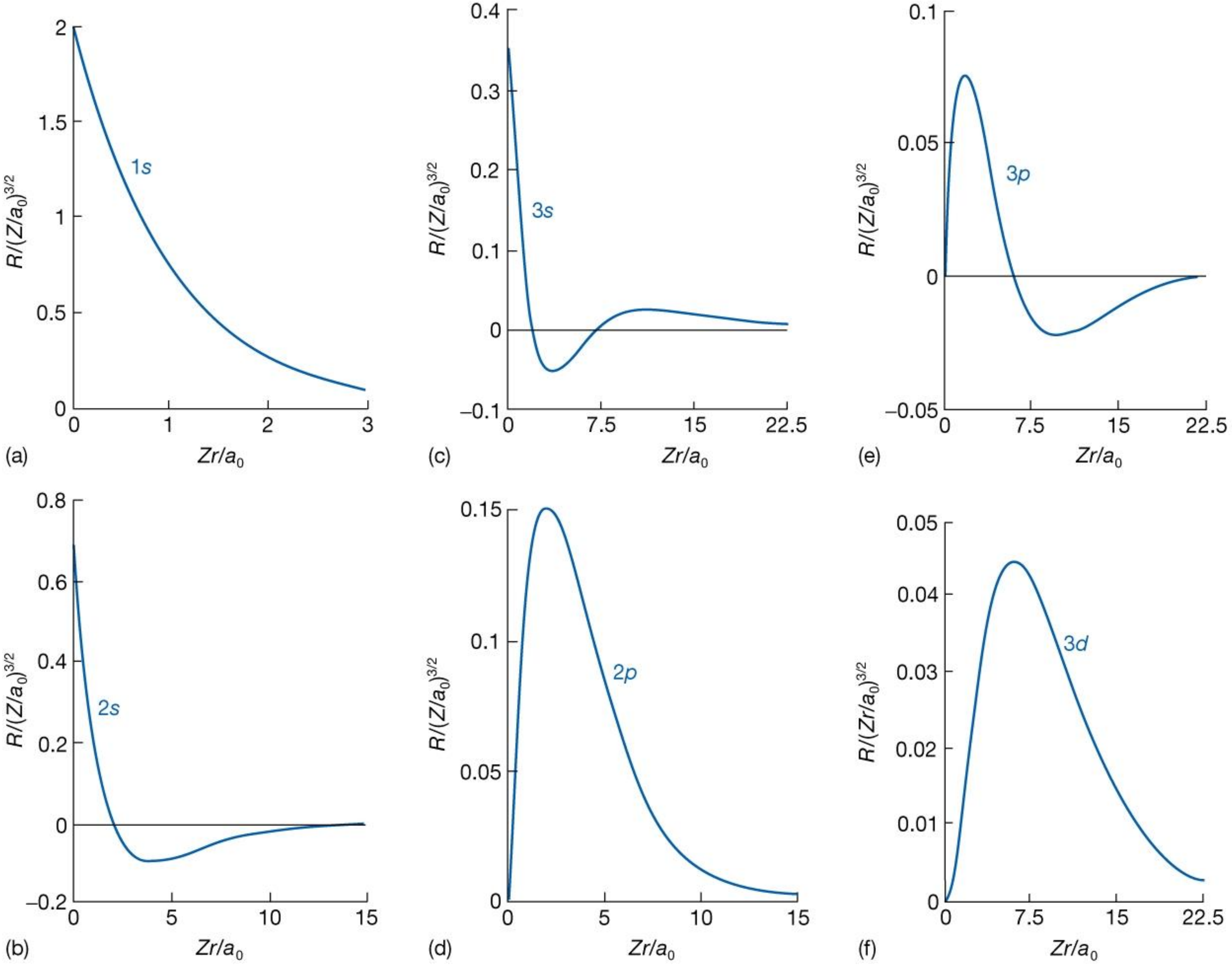
$$\rho=\frac{2zr}{na_0},\quad a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$ (與其他參考書有些不同,須注意)

$$E_n=-\frac{z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2},\quad n=1,2,3\cdots,\ E_n=-\frac{hcR_H}{n^2},\ 而\ hcR_H=\frac{z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

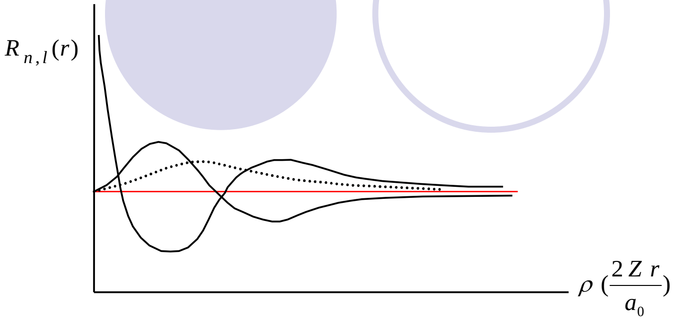
Table 9A.1， p361

Orbital	n	ℓ	$R_{n,\ell}(r)$
$1s$	1	0	$2(\frac{z}{a_0})^{3/2}e^{-\rho/2}$
$2s$	2	0	$\frac{1}{(8)^{1/2}}(\frac{z}{a_0})^{3/2}(2-\rho)e^{-\rho/2}$
$2p$	2	1	$\frac{1}{(24)^{1/2}}(\frac{z}{a_0})^{3/2}\rho e^{-\rho/2}$
$3s$	3	0	$\frac{1}{(243)^{1/2}}(\frac{z}{a_0})^{3/2}(6-6\rho+\rho^2)e^{-\rho/2}$

其中 $R_{n,\ell}(r)$ 形狀。列於 Fig 9.5, p361


(a)
R/(Z/a_0)^{3/2}
2
1.5
1
0.5
0
0
1
2
3
1s
Zr/a_0
(b)
R/(Z/a_0)^{3/2}
0.8
0.6
0.4
0.2
0
–0.2
0
5
10
15
2s
Zr/a_0
(c)
R/(Z/a_0)^{3/2}
0.4
0.3
0.2
0.1
0
–0.1
0
7.5
15
22.5
3s
Zr/a_0
(d)
R/(Z/a_0)^{3/2}
0.15
0.1
0.05
0
0
5
10
15
2p
Zr/a_0
(e)
R/(Z/a_0)^{3/2}
0.1
0.05
0
–0.05
0
7.5
15
22.5
3p
Zr/a_0
(f)
R/(Zr/a_0)^{3/2}
0.05
0.04
0.03
0.02
0.01
0
0
7.5
15
22.5
3d
Zr/a_0

9.2 Atomic orbital and their energies

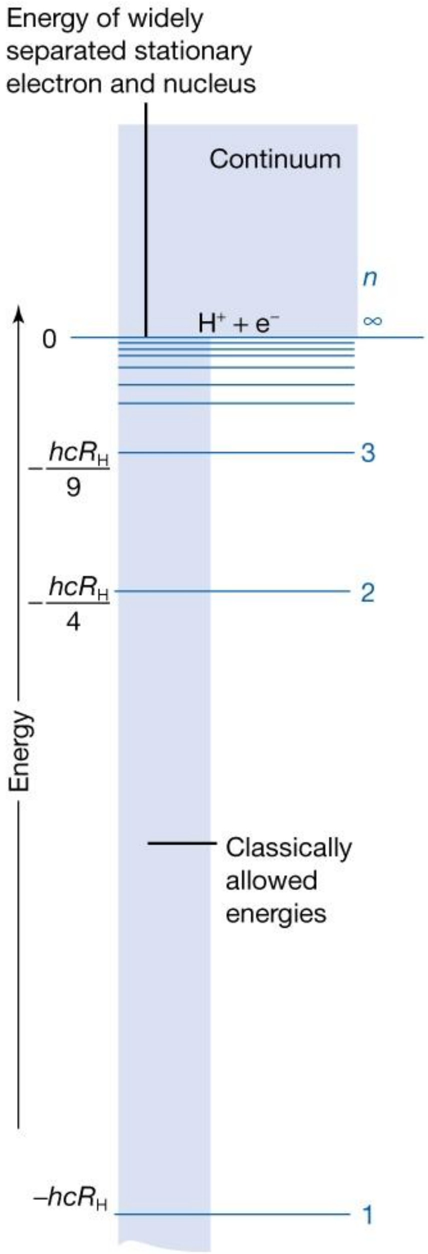


注意之處是，當 $R_{n,\ell}(r)_{r=0}=0$, 其 node 的數目與 n,ℓ 關係。

Which graph corresponds to which set of (*n*,*l*)?

Energy levels：由 schrödinger equation 解得. $E_n=-\dfrac{hcR_H}{n^2}$

對所有 n, E_n 皆為負值，代表這些 states 皆為 bound states；然而在所得解中，也有正值，但那些值並非 quantized，稱 unbound states。是連續的，又稱為 continuum states。


Energy of widely separated stationary electron and nucleus
Continuum
n
H$^+$ + e$^-$
∞
0
$-\frac{hcR_H}{9}$
3
$-\frac{hcR_H}{4}$
2
Energy
Classically allowed energies
$-hcR_H$
1

Ionization energy：將電子從 E_1 打到 continuum states 所需的最小能量

$$\therefore \Delta E = 0 - E_1 = hcR_H = 2.18\times10^{-18}\ J = 13.60\ eV$$

如何從光譜上看出 ？ (series limit see fig 13.6 , p351.)

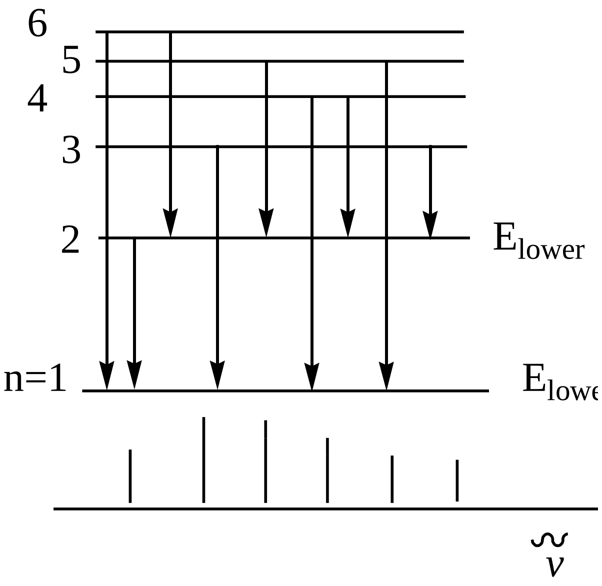
在數學上的處理：

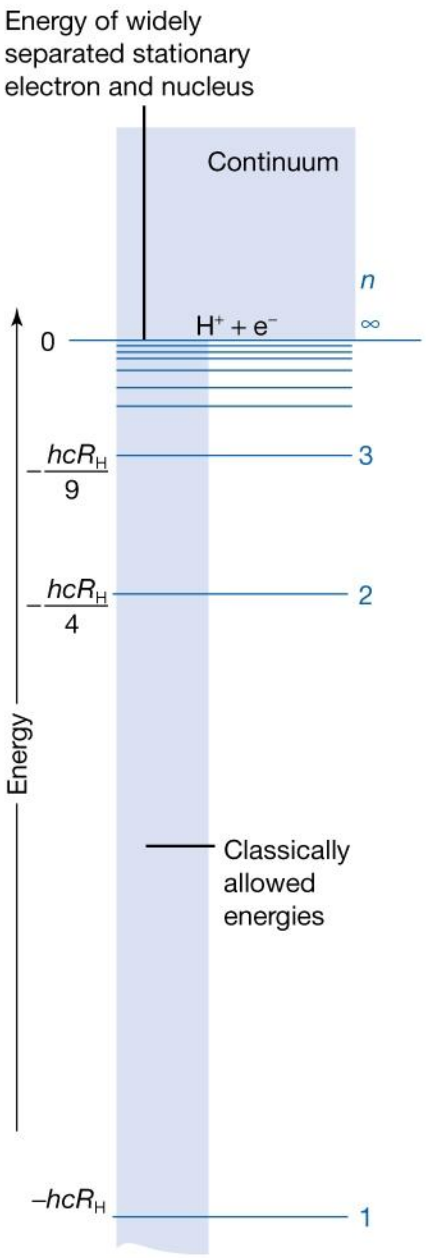
$$\Delta E = E_{upper} - E_{lower}$$

$$h\nu = \frac{-hcR_H}{n^2} - E_{lower},$$

$$\therefore \text{除} hc$$

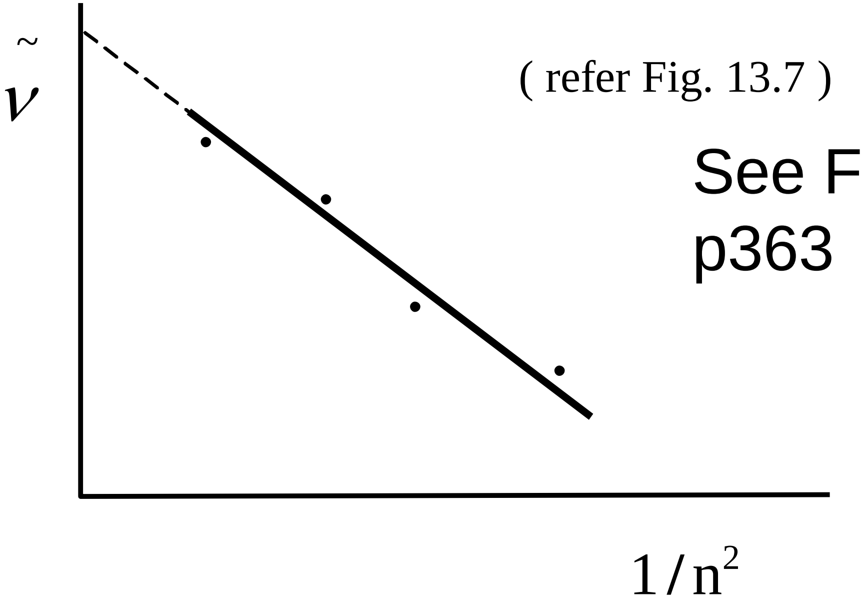
$$\tilde{\nu} = \frac{-R_H}{n^2} - \frac{E_{lower}}{hc}$$





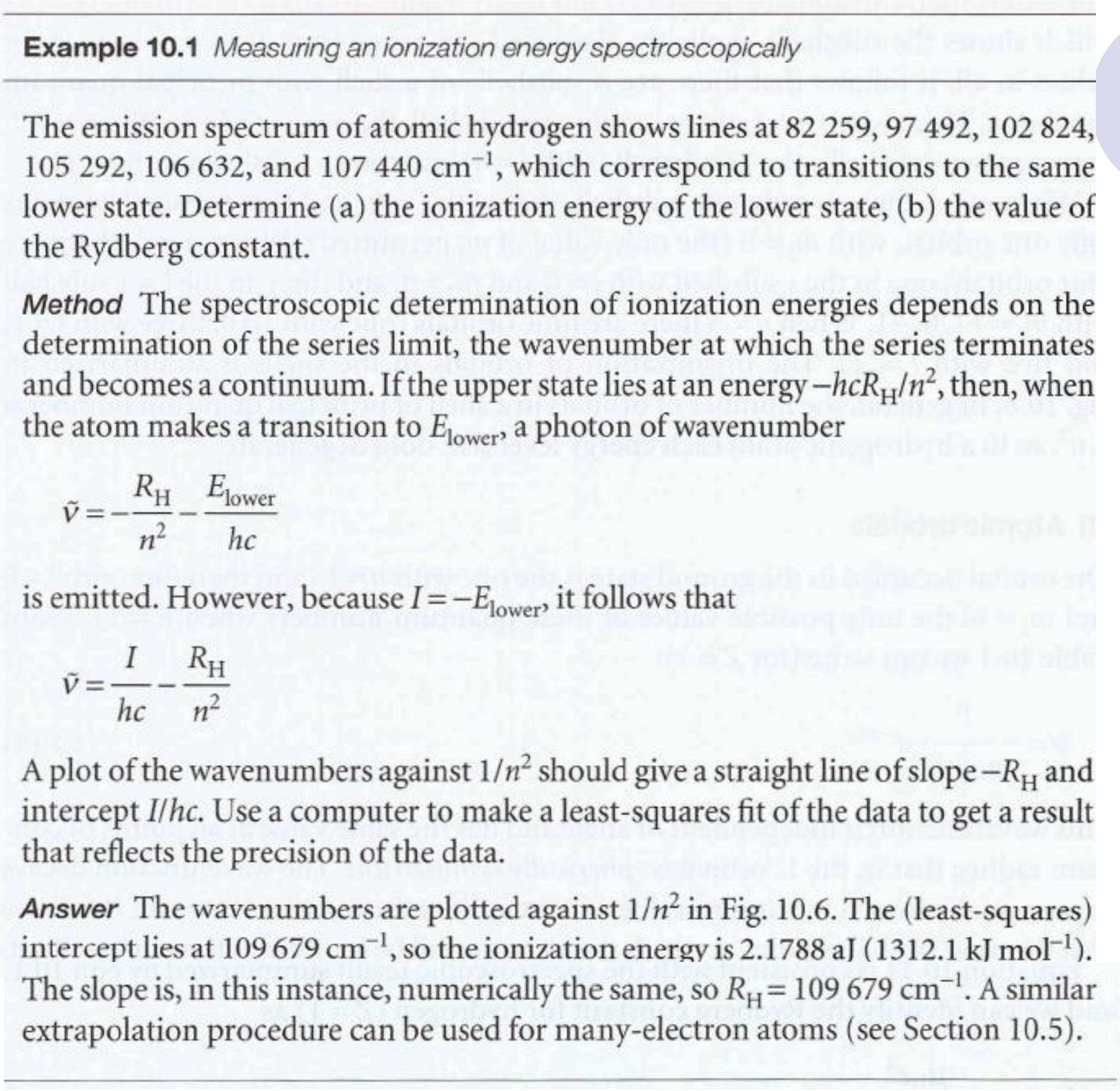
Example 9.1

由譜線的位置，$\tilde{\nu}$ 對 $1/n^2$ 做圖得一直線，斜率為負值($-R_H$)，截距為 $-\frac{E_{lower}}{hc}$，表示可得 lower state 的 ionization energy .(從 n=2, 3, 4, 5,…or n=3, 4, 5, 6,……or n=4, 5, 6,…) 視何者可成一直線，而決定該譜圖的 lower state，再用外插法求出截距與 ground state(n=1)的 ionization energy .



(refer Fig. 13.7)

See Fig.9A.7 p363



Example 10.1 *Measuring an ionization energy spectroscopically*

The emission spectrum of atomic hydrogen shows lines at 82 259, 97 492, 102 824, 105 292, 106 632, and 107 440 cm^{-1}, which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the value of the Rydberg constant.

Method The spectroscopic determination of ionization energies depends on the determination of the series limit, the wavenumber at which the series terminates and becomes a continuum. If the upper state lies at an energy $-hcR_H/n^2$, then, when the atom makes a transition to E_{lower}, a photon of wavenumber

$$\tilde{\nu} = -\frac{R_H}{n^2} - \frac{E_{\text{lower}}}{hc}$$

is emitted. However, because $I = -E_{\text{lower}}$, it follows that

$$\tilde{\nu} = \frac{I}{hc} - \frac{R_H}{n^2}$$

A plot of the wavenumbers against $1/n^2$ should give a straight line of slope $-R_H$ and intercept I/hc. Use a computer to make a least-squares fit of the data to get a result that reflects the precision of the data.

Answer The wavenumbers are plotted against $1/n^2$ in Fig. 10.6. The (least-squares) intercept lies at 109 679 cm^{-1}, so the ionization energy is 2.1788 aJ (1312.1 kJ mol^{-1}). The slope is, in this instance, numerically the same, so $R_H = 109\,679\ \text{cm}^{-1}$. A similar extrapolation procedure can be used for many-electron atoms (see Section 10.5).

WavefNs：

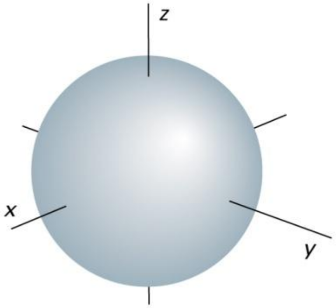
$$\psi(r,\theta,\phi)=R_{n,\ell}(r)\cdot Y_{\ell,m_\ell}(\theta,\phi)$$
$$=(radial\ \ part)(angular\ \ part)$$

Radial part：與能量有關(associated Laguerre polynomial)隨 r 增加而decay

Angular part：與空間的方向(向位、形狀)有關 (associated Legendre polynomial)

一般畫圖顯示時,以電子出現機率總和達90%的範圍畫出，之外就不表示了，該範圍含蓋電子90%出現機率，稱為 boundary surface。

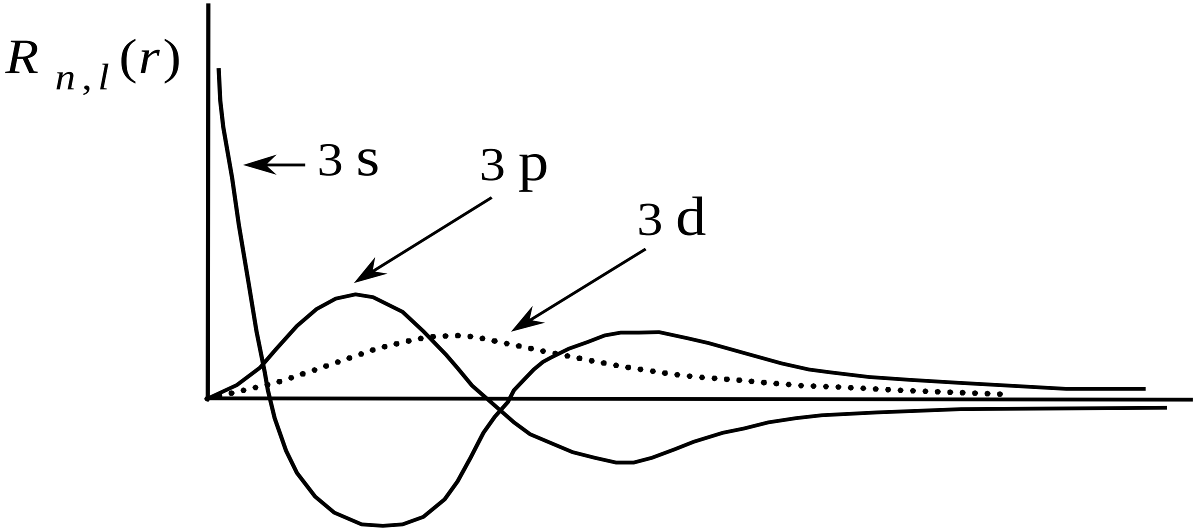
(如Fig9A.11, 9A.12, p365)



畫出wavefN時,有多種表示法:

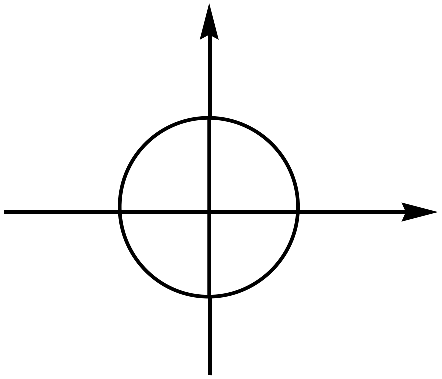
(1)僅表示radial part, $R_{n,\ell}(r)$ Vs. r

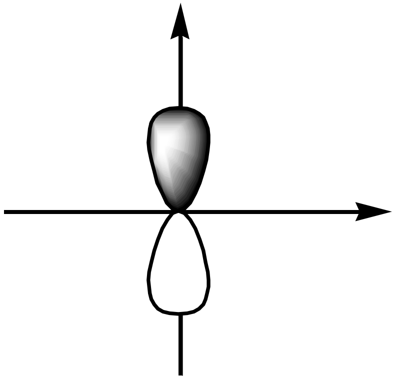
(表示出節點及 $e^{-\rho/2n}$ 的decay關係)



(2)僅表示angular part,

$$Y_{\ell,\,m}(\theta,\phi)$$


s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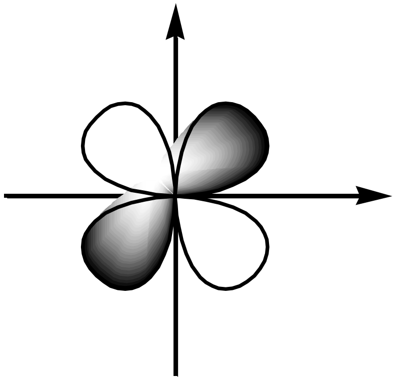
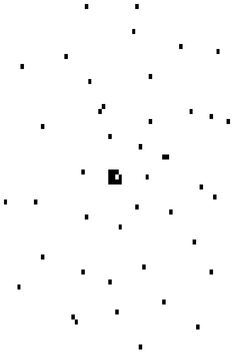
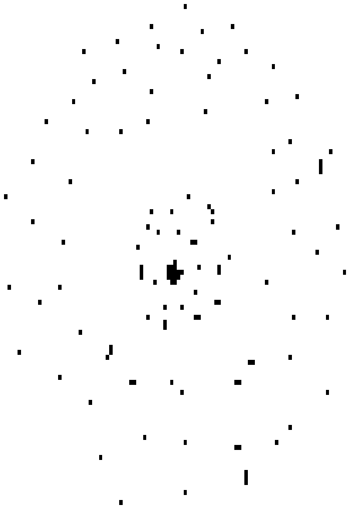

d

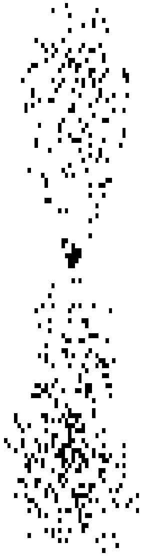
(3)兩者一起表示，以點的密集度表示 r 越大時，其radial part的 $e^{-\rho/2n}$ 的decay及angular part的形狀。



1s

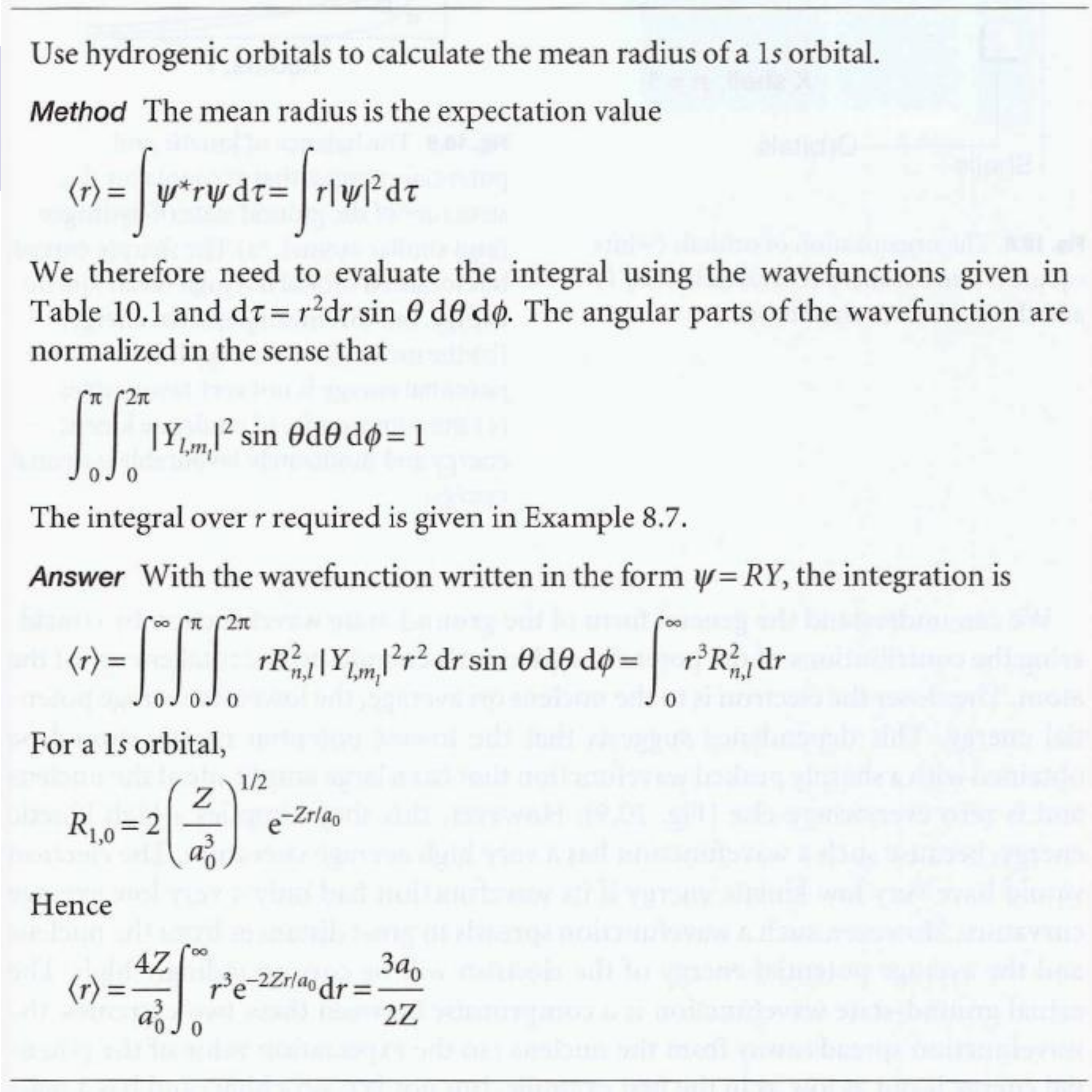


2s (有1個node)



2p

3p (有1個node)



Use hydrogenic orbitals to calculate the mean radius of a 1*s* orbital.

Method The mean radius is the expectation value

$$\langle r\rangle = \int \psi^* r \psi \, \mathrm{d}\tau = \int r|\psi|^2 \, \mathrm{d}\tau$$

We therefore need to evaluate the integral using the wavefunctions given in Table 10.1 and $\mathrm{d}\tau = r^2 \mathrm{d}r \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$. The angular parts of the wavefunction are normalized in the sense that

$$\int_0^{\pi}\int_0^{2\pi} |Y_{l,m_l}|^2 \sin\theta \mathrm{d}\theta \, \mathrm{d}\phi = 1$$

The integral over *r* required is given in Example 8.7.

Answer With the wavefunction written in the form $\psi = RY$, the integration is

$$\langle r\rangle = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} rR_{n,l}^2 |Y_{l,m_l}|^2 r^2 \, \mathrm{d}r \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = \int_0^{\infty} r^3 R_{n,l}^2 \, \mathrm{d}r$$

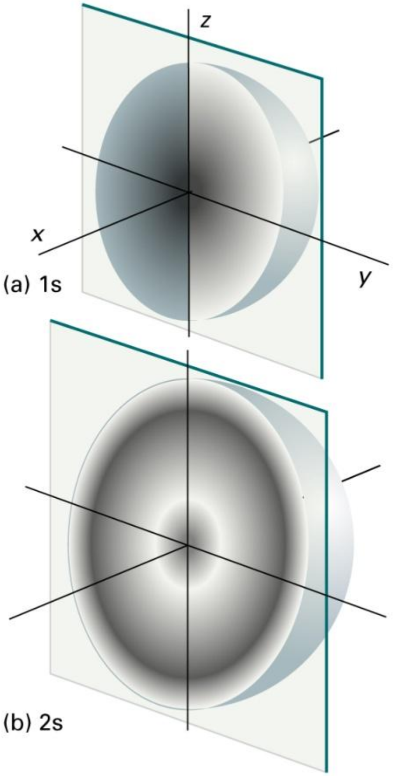
For a 1*s* orbital,

$$R_{1,0} = 2\left(\frac{Z}{a_0^3}\right)^{1/2} \mathrm{e}^{-Zr/a_0}$$

Hence

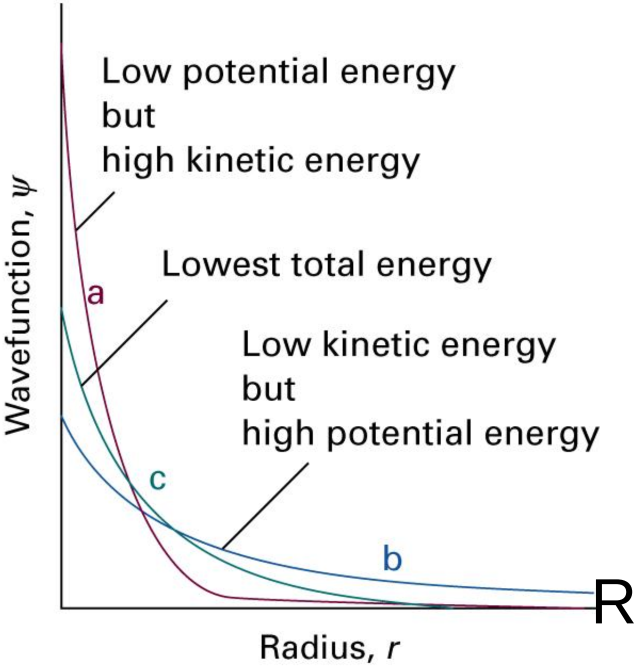
$$\langle r\rangle = \frac{4Z}{a_0^3}\int_0^{\infty} r^3 \mathrm{e}^{-2Zr/a_0} \mathrm{d}r = \frac{3a_0}{2Z}$$

S orbital



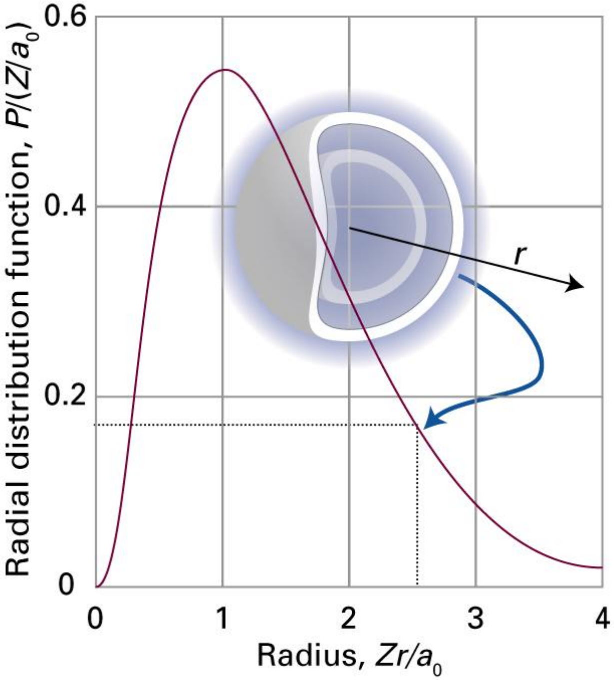
Spherical symmetry

$$\psi = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$



Energetics

$$P(r) = 4\pi r^2 \psi^2 = r^2 R(r)^2$$



Radial distribution function

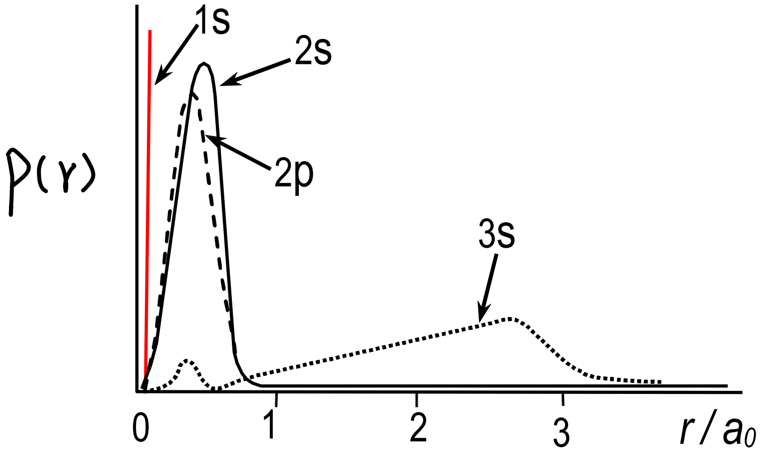
$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

$$\frac{dP}{dr} = \frac{4Z^3}{a_0^3}\left(2r - \frac{2Zr^2}{a_0}\right) e^{-2Zr/a_0}$$

$$r^* = \frac{a_0}{Z}$$

Radial distribution fNs：$P(r)$

Give the probability density that the electron will be found anywhere in a shell of radius r.基本上只與 r 有關, 除非特別指定有方向性的 orbital。因此其為球形對稱, 為在某一 r 的 dr 殼層厚度球體表面出現的概率。

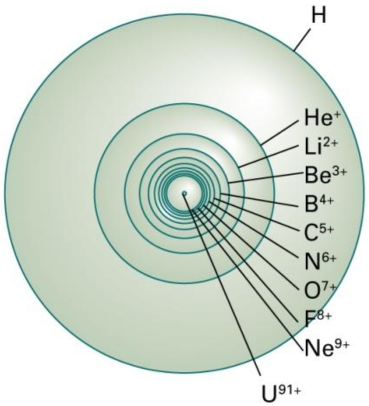


$$P(r)dr = \int_0^{\pi}\int_0^{2\pi} R(r)^2 |Y(\theta,\phi)|^2 r^2 dr \sin\theta \, d\theta d\phi$$

$$= r^2 R(r)^2 dr \int_0^{\pi}\int_0^{2\pi} |Y(\theta,\phi)|^2 \sin\theta \, d\theta d\phi$$

$$= r^2 R(r)^2 dr$$

probability $= \int P(r) dr$ $\quad \therefore P(r) = r^2 R(r)^2$



Radial distribution fN 補充:

對spherical orbital 而言.

$$\Psi(r,\theta,\phi) = R(r)$$

$$\therefore P(r)dr = \int_0^{2\pi}\int_0^{\pi} R^2(r) r^2 dr \sin\theta \; d\theta \; d\phi = R^2(r) r^2 dr \int \sin\theta \; d\theta \int d\,\phi$$

$$= 4\pi r^2 R^2(r)\, dr$$

對非*spherical orbital*而言 $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

$$p(r)\,dr = \int_0^{2\pi}\int_0^{\pi} R^2(r) \left|Y(\theta,\phi)\right|^2 r^2 \sin\theta \; d\theta \; d\phi \; dr$$

$$= r^2 R^2(r)\, dr \int_0^{\pi}\int_0^{2\pi} \left|Y(\theta,\phi)\right|^2 \sin\theta \, d\theta \, d\phi$$

$$= r^2 \; R^2(r)\, dr$$

$\because \Psi$為*normalized fN*

$$\therefore \int\int \left|Y(\theta,\phi)\right|^2 \sin\theta \; d\theta \; d\phi = 1$$

The most probable radius r_{mp}.

e.g. Calculate the most probable radius r_{mp}, at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z.

已知

$$\Psi_{1s} = \left(\frac{z^3}{\pi a_\circ^{\,3}} \right)^{1/2} e^{-zr/a_\circ} \quad (normalized)$$

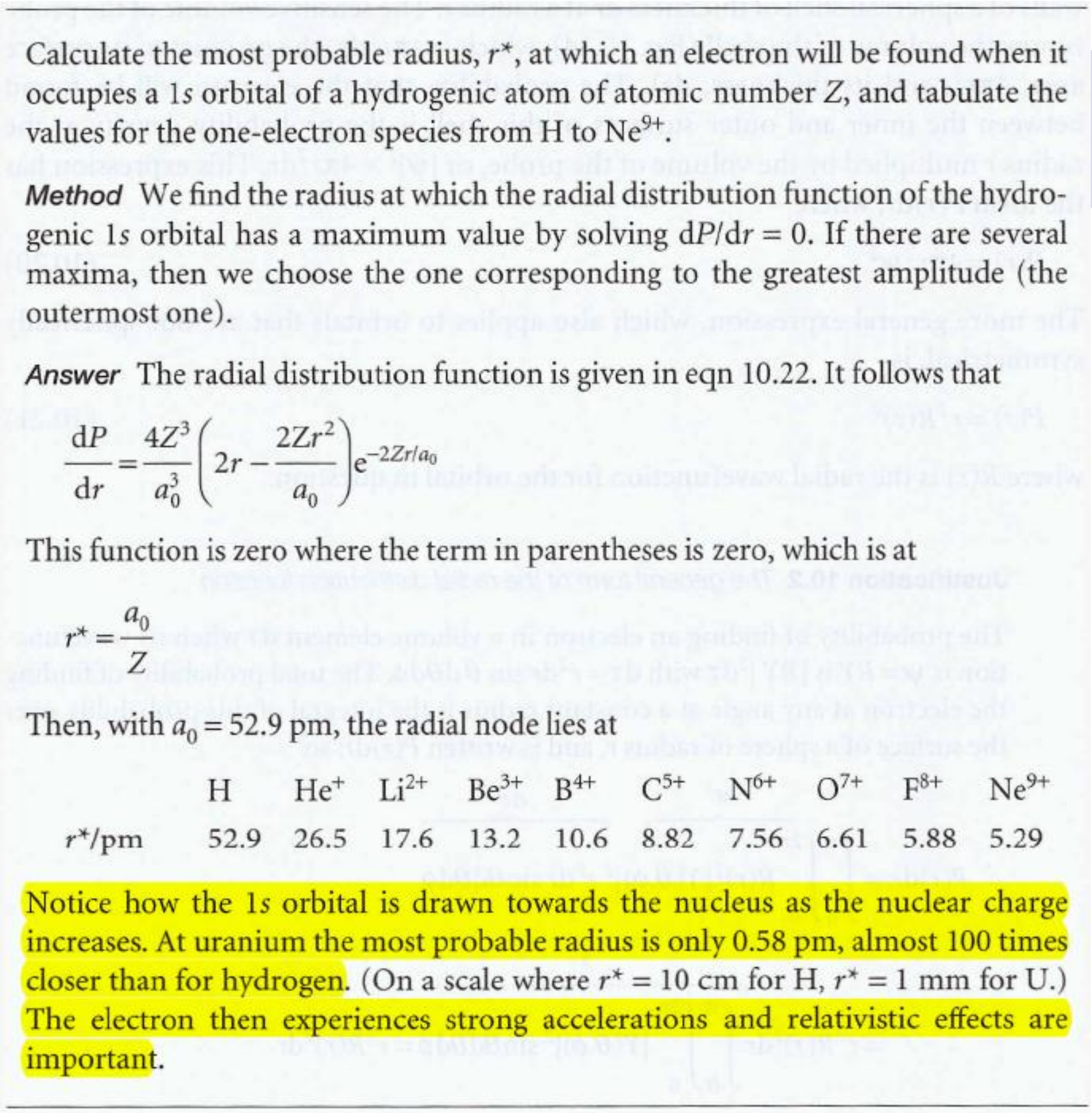
解: 先求出p(r) for 1s orbital球形對稱

$$p(r) = 4\pi r^2 \Psi^2 = 4\pi r^2 \left(\frac{z^3}{\pi a_\circ^3}\right) e^{-2zr/a_\circ}$$

$$\frac{d\,p(r)}{dr} = 4\pi \cdot \left(\frac{z^3}{\pi a_\circ^3}\right)\left(2r - \frac{2zr^2}{a_\circ}\right) e^{\frac{-2zr}{a_\circ}} = 0$$

$$\therefore\ 2r - \frac{2zr^2}{a_0} = 0 \qquad \therefore\ r\left(2 - \frac{2zr}{a\circ}\right) = 0$$

$$\therefore\ r_{mp} = \frac{a_\circ}{z} \qquad (\text{當}\, z = 1 \text{時, 即為} \mathit{Bohr\ radius})$$



Calculate the most probable radius, r^*, at which an electron will be found when it occupies a 1*s* orbital of a hydrogenic atom of atomic number Z, and tabulate the values for the one-electron species from H to Ne^{9+}.

Method We find the radius at which the radial distribution function of the hydrogenic 1*s* orbital has a maximum value by solving $\mathrm{d}P/\mathrm{d}r = 0$. If there are several maxima, then we choose the one corresponding to the greatest amplitude (the outermost one).

Answer The radial distribution function is given in eqn 10.22. It follows that

$$\frac{\mathrm{d}P}{\mathrm{d}r} = \frac{4Z^3}{a_0^3}\left(2r - \frac{2Zr^2}{a_0}\right)\mathrm{e}^{-2Zr/a_0}$$

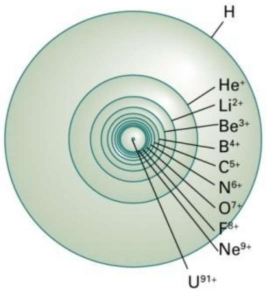
This function is zero where the term in parentheses is zero, which is at

$$r^* = \frac{a_0}{Z}$$

Then, with $a_0 = 52.9$ pm, the radial node lies at

	H	He^+	Li^{2+}	Be^{3+}	B^{4+}	C^{5+}	N^{6+}	O^{7+}	F^{8+}	Ne^{9+}
r^*/pm	52.9	26.5	17.6	13.2	10.6	8.82	7.56	6.61	5.88	5.29

Notice how the 1*s* orbital is drawn towards the nucleus as the nuclear charge increases. At uranium the most probable radius is only 0.58 pm, almost 100 times closer than for hydrogen. (On a scale where $r^* = 10$ cm for H, $r^* = 1$ mm for U.) The electron then experiences strong accelerations and relativistic effects are important.



求 *mean radius*

$$<r>=\int_0^\infty \Psi^* \,\hat{r}\, \Psi \, d\tau \qquad \Psi = R_{n,\ell}(r)Y_{\ell,m}(\theta,\phi) \quad (normalized)$$

$$=\int r|\Psi|^2 \, d\tau = \int r\, R^2{}_{n,\ell}(r) r^2 dr \int |Y_{\ell,m}(\theta,\phi)|^2 \sin\theta \, d\theta \, d\phi$$

$$=\int_0^\infty r^3 R^{\,2}_{\,n,\ell}(r)\, dr \qquad (\because \Psi\text{是}normalized, \ \therefore \int |Y_{\ell,m}(\theta,\phi)|^2 \sin\theta \, d\theta \, d\phi = 1)$$

$$<r>_{n,\ell} = n^2\left\{1+\frac{1}{2}\left(1-\frac{\ell(\ell+1)}{n^2}\right)\right\}\frac{a_\circ}{Z}$$

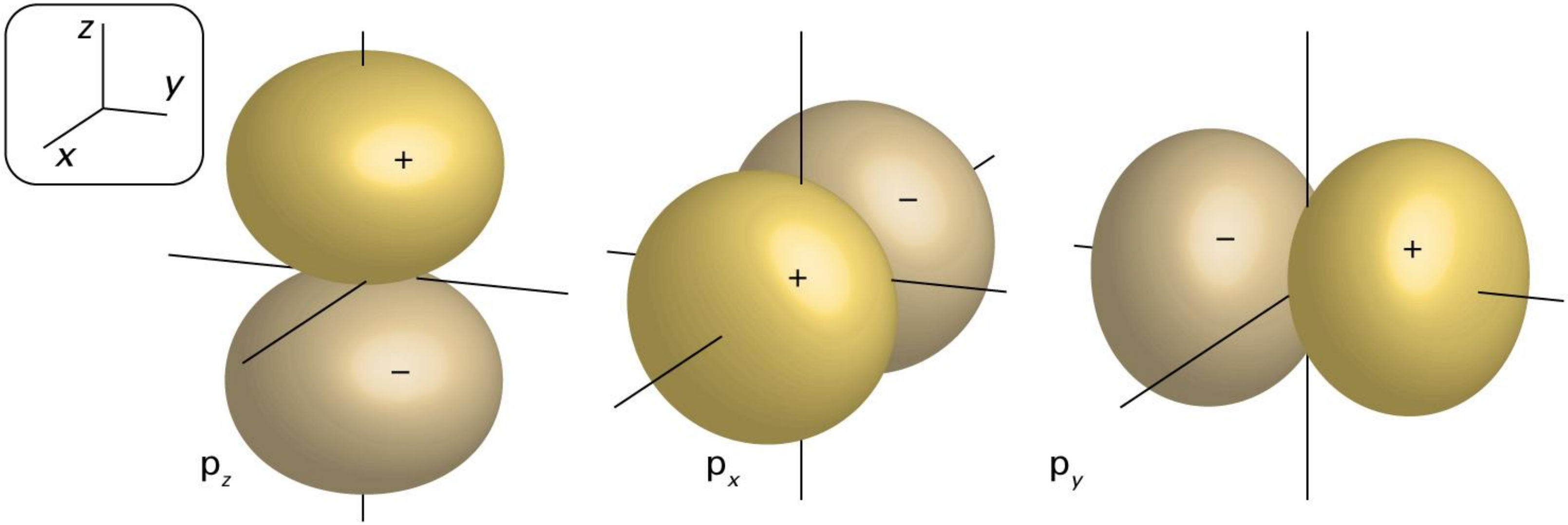
<r> > 0,

<r>↑, Z↓, l↓, n↑

p orbital

$$\psi_{p_0} = R_{2,1}(r)Y_{1,0}(\theta,\phi) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta\, e^{-Zr/2a_0}$$
$$= r\cos\theta f(r)$$

1. $m_l = 0$, no imaginary $e^{im\phi}$
2. $m_l = 0$, no component in xy-plane



$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi f(r) = xf(r)$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r\sin\theta\sin\phi f(r) = yf(r)$$

對於具有虛數的 wavefN（如 p_{+1} , p_{-1} , $d_{\pm 1}$, $d_{\pm 2}$ ）在以圖形表達時要如何處理?

e.g.

$$\Psi_{2p+1} = \underset{\text{實數}}{\underline{\underline{R_{2,1}(r)}}}\ \underset{\text{虛數}}{\underline{\underline{Y_{1,+1}(\theta,\phi)}}} = -\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_\circ}\right)^{5/2} r e^{-Zr/2a_\circ}\sin\theta\, e^{+i\phi} \quad \propto \quad r\sin\theta\, e^{+i\phi}$$

$$\Psi_{2p-1} = \underline{\underline{R_{2,1}(r)}}\ \underline{\underline{Y_{1,-1}(\theta,\phi)}} = +\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_\circ}\right)^{5/2} r e^{-Zr/2a_\circ}\sin\theta\, e^{-i\phi} \quad \propto \quad r\sin\theta\, e^{-i\phi}$$

∵ 該二個orbitals互為degenerate,

∴ 可以做 linear combination，得到的新的orbital 其能量仍然不變。可以用此法消去虛數部分。

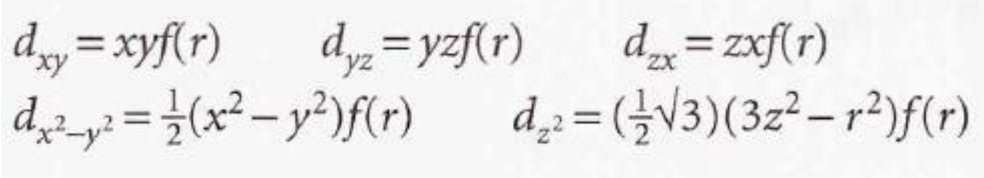
e.g.

令 $\Psi_{2p_x} = -\frac{1}{\sqrt{2}}\left(\Psi_{2p+1} \boxed{-} \Psi_{2p-1}\right) \propto r\sin\theta\cos\phi \to$ 在X軸上

令 $\Psi_{2p_y} = \frac{i}{\sqrt{2}}\left(\Psi_{2p+1} \boxed{+} \Psi_{2p-1}\right) \propto r\sin\theta\sin\phi \to$ 在Y軸上

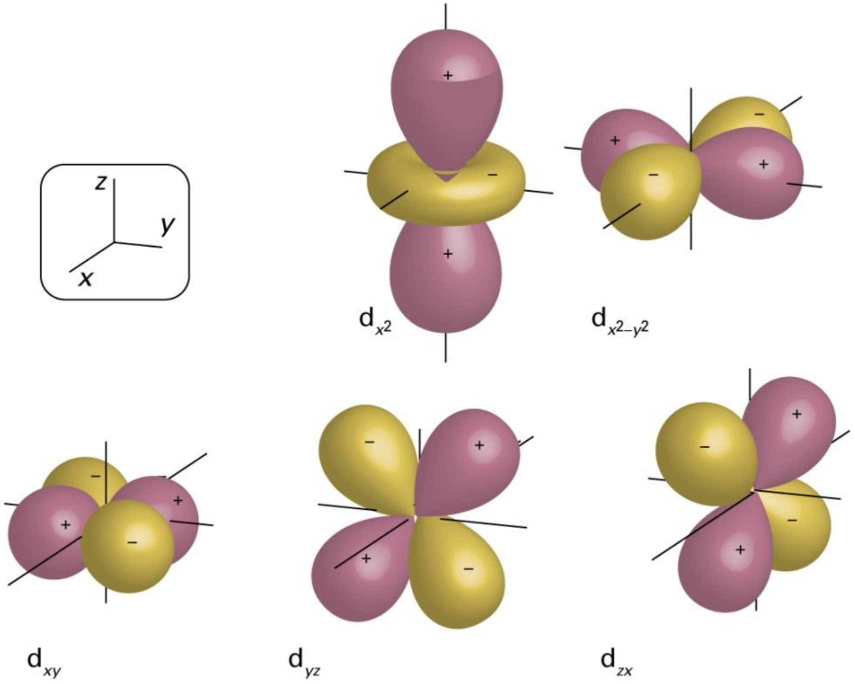
∴原來解出的 $2P_0, 2P_{+1}, 2P_{-1}$ 就可以 $2P_z, 2P_x, 2P_y$來表示

同理 $d_{\pm1}, d_{\pm2}, d_0$ 亦可用此法以$d_{xz}, d_{yz}, d_{x^2-y^2}, d_{yx}, d_{z^2}$表示



$d_{xy} = xyf(r) \qquad d_{yz} = yzf(r) \qquad d_{zx} = zxf(r)$

$d_{x^2-y^2} = \frac{1}{2}(x^2-y^2)f(r) \qquad d_{z^2} = (\frac{1}{2}\sqrt{3})(3z^2-r^2)f(r)$



Spectroscopic transitions and selection rules:

$$\Delta\ell = \pm 1, \qquad \Delta m_\ell = 0, \pm 1$$

主要是由$evaluate\ transition dipole\ moment, \mu_{fi},$而得

$\mu_{fi} = \langle f | \mu | i \rangle,$ 當$\mu_{f\,i} \neq 0,$ 則$transition$可發生

當$\mu_{f\,i} = 0,$ 則$transition$不可發生

$f \Rightarrow\ final state wave fN,\ \Psi_f$

$i \Rightarrow\ initial state wave fN,\ \Psi_i$

$$\mu_{\mathrm{fi}} = \langle \mathrm{f}|\mu|\mathrm{i}\rangle$$

$$\mu_{z,\mathrm{fi}} = -e\langle \mathrm{f}|z|\mathrm{i}\rangle = -e\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}}\, \mathrm{d}\tau$$

$$\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}} \mathrm{d}\tau = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \overbrace{R_{n_{\mathrm{f}},l_{\mathrm{f}}} Y^{*}_{l_{\mathrm{f}},m_{l,\mathrm{f}}}}^{\psi_{\mathrm{f}}} \overbrace{\left(\frac{4\pi}{3}\right)^{1/2} r Y_{1,0}}^{z} \overbrace{R_{n_{\mathrm{i}},l_{\mathrm{i}}} Y_{l_{\mathrm{i}},m_{l,\mathrm{i}}}}^{\psi_{\mathrm{i}}} \overbrace{r^2 \mathrm{d}r \sin\theta \mathrm{d}\theta \mathrm{d}\phi}^{\mathrm{d}\tau}$$

$$\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}} \mathrm{d}\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^{\infty} R_{n_{\mathrm{f}},l_{\mathrm{f}}} r R_{n_{\mathrm{i}},l_{\mathrm{i}}} r^2 \mathrm{d}r \int_0^{\pi}\int_0^{2\pi} Y^{*}_{l_{\mathrm{f}},m_{l,\mathrm{f}}} Y_{1,0} Y_{l_{\mathrm{i}},m_{l,\mathrm{i}}} \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$

$$\int_0^{\pi}\int_0^{2\pi} Y^{*}_{l_{\mathrm{f}},m_{l_{\mathrm{f}}}} Y_{1,m} Y_{l_{\mathrm{i}},m_{l_{\mathrm{i}}}} \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$

$\Delta l = \pm 1$ and $\Delta m_l = 0$

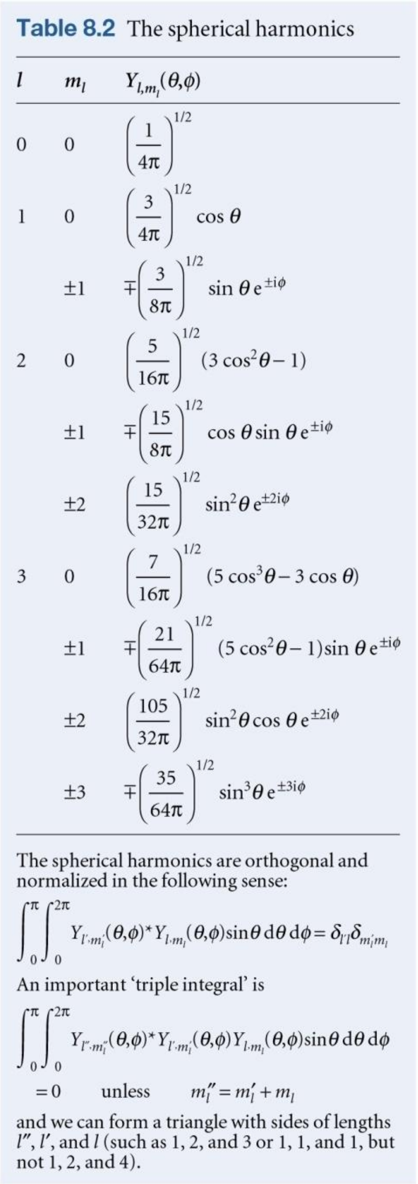


Table 8.2 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta\, \mathrm{e}^{\pm \mathrm{i}\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, \mathrm{e}^{\pm 2\mathrm{i}\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2} (5\cos^2\theta - 1)\sin\theta\, \mathrm{e}^{\pm \mathrm{i}\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta\, \mathrm{e}^{\pm 2\mathrm{i}\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta\, \mathrm{e}^{\pm 3\mathrm{i}\phi}$

The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^{\pi}\int_0^{2\pi} Y_{l',m_l'}(\theta,\phi)^{*} Y_{l,m_l}(\theta,\phi) \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi = \delta_{l'l}\delta_{m_l'm_l}$$

An important 'triple integral' is

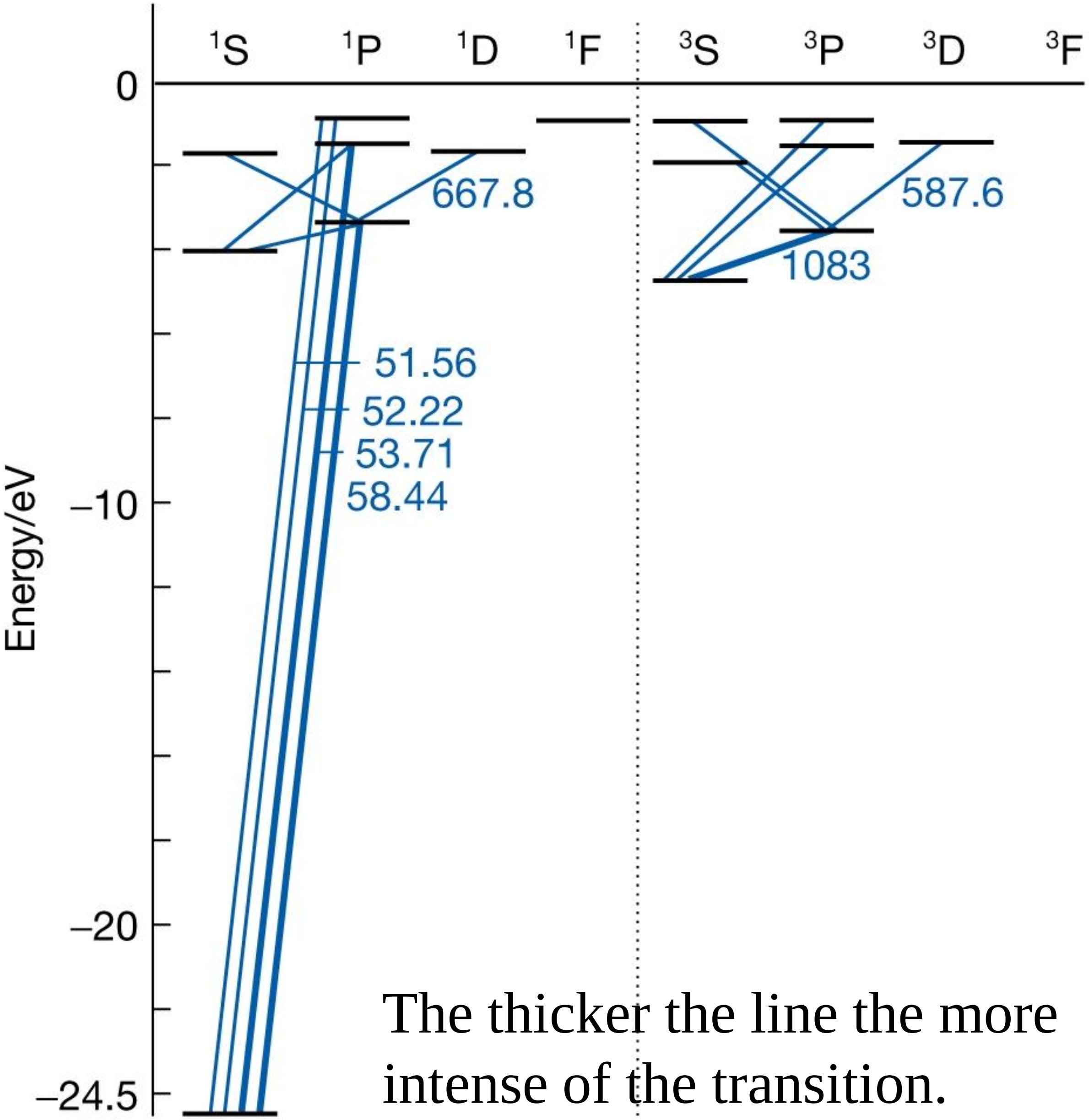
$$\int_0^{\pi}\int_0^{2\pi} Y_{l'',m_l''}(\theta,\phi)^{*} Y_{l',m_l'}(\theta,\phi) Y_{l,m_l}(\theta,\phi) \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi$$

$$= 0 \qquad \text{unless} \qquad m_l'' = m_l' + m_l$$

and we can form a triangle with sides of lengths l'', l', and l (such as 1, 2, and 3 or 1, 1, and 1, but not 1, 2, and 4).

一般而言，因為光子的intrinsic spin, s=1. 當光子是由於電子的躍遷而產生時，必會失去一個angular momentum。 因此其所能躍遷的orbital的變化，只能為s到p軌域不可為s到s軌域，同理s軌域不可到d軌域。因此有所謂的allow or forbidden的區別。

Grotrian diagram 顯示躍遷的途徑與光譜 fig 9.17 p340



The thicker the line the more intense of the transition.

The structure of many-electron atoms

- 要解多電子原子的 wavefN 是件很複雜的難題，電子間彼此相互作用很難精確算出，因此必須用approximate的方法，即使 He原子只有2個電子，至今尚無法用一完整式子來描述它們的軌域與能量關係。

Orbital approximation

- 假設多電子原子的wavefN, $\boxed{\Psi(r_1,r_2,r_3,\ldots)=\Psi(r_1)\Psi(r_2)\Psi(r_3)\ldots\ldots}$
- 其中每個$\boxed{\Psi(r_i)}$皆類似氫原子電子(hydrogenic atom)的wavefN但其核以其它電子皆在該核上的假設來修正(亦即考慮為effective nuclear charge而非真正質子數))。

e.g. For He atom 令

$\Psi(r_1, r_2) = \Psi(r_1)\,\Psi(r_2)$，並令 $\hat{\mathrm{H}} = \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2$

(忽略了二個電子的 *interaction*)

則 $\hat{\mathrm{H}}\Psi(r_1, r_2) = (\hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2)\,\Psi(r_1)\Psi(r_2)$

$$= \hat{\mathrm{H}}_1\Psi(r_1)\Psi(r_2) + \hat{\mathrm{H}}_2\Psi(r_2)\Psi(r_1)$$

$$= E_1\,\Psi(r_1)\Psi(r_2) + E_2\Psi(r_1)\Psi(r_2) = (E_1 + E_2)\,\Psi(r_1)\Psi(r_2)$$

$$= E\,\Psi(r_1)\Psi(r_2)\,,$$ 其中 $E = E_1 + E_2$

事實上，電子間存在有相互作用力，所以此法只是一種 *approximation*
然而它允許我們用來表示電子的結構 (*configuration*)

e.g. He的電子組態寫成 $1s^2$， Li: $1s^2 2s^1$

Pauli principle:

When the labels of any two identical fermions are exchanged, the total wavefN changes sign, when the labels of any two identical bosons are exchanged, the total wavefN retains the same sign.

說明：對fermion而言，例如電子，若有兩個電子填入一相同軌域，其wavefN為 $\Psi \rightarrow \Psi(1,2)$

依據Pauli principle $\Psi(1, 2) = -\Psi(2, 1)$

只有具此性質的wavefN才被接受，包括spatial part and spin part。

spin 填法有如下四種 $\alpha(1)\alpha(2),\ \beta(1)\beta(2),\ \alpha(1)\beta(2),\ \beta(1)\alpha(2)$

後兩種因無法得知那個電子是α，那個是 β

因此以另兩種表示法來表示比較正確：

$$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right);\quad \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)-\beta(1)\alpha(2)\right)$$

現與spatial part，$\Psi_x(1)\Psi_x(2)$(含蓋radial and angular part)，相結合:

$$\psi_\chi(1,2)=\psi_\chi(1)\psi_\chi(2)\alpha(1)\alpha(2);\ \text{而}\ \psi_\chi(2,1)=\psi_\chi(2)\psi_\chi(1)\alpha(2)\alpha(1)$$

$$\psi_\chi(1,2)=\psi_\chi(1)\psi_\chi(2)\beta(1)\beta(2);\ \text{而}\ \psi_\chi(2,1)=\psi_\chi(2)\psi_\chi(1)\beta(2)\beta(1)$$

$$\psi_\chi(1,2)=\psi_\chi(1)\psi_\chi(2)\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\};\ \text{而}\ \psi_\chi(2,1)=\psi_\chi(2)\psi_\chi(1)\{\alpha(2)\beta(1)+\beta(2)\alpha(1)\}$$

$$\psi_\chi(1,2)=\psi_\chi(1)\psi_\chi(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\};\ \text{而}\ \psi_\chi(2,1)=\psi_\chi(2)\psi_\chi(1)\{\alpha(2)\beta(1)-\beta(2)\alpha(1)\}$$

前三種case $\psi_x(1,2)=\psi_x(2,1)$ 亦即total wavefN sign不變，只有最後一種

$$\psi_x(1,2)=-\psi_x(2,1)$$

因此依據Pauli principle (電子是fermion)，其allowed wavefN ,必須是

$$\psi_x(1,2)=\psi_x(1)\psi_x(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

這結果也說明了，若兩個電子填入相同orbital，其spins必須是paired（這就是Pauli excluding principle所說的）。

若一wavefN含有多個電子， $\psi(1,2,3,\cdots)$

其仍然必須符合Pauli principle，交換任何兩個電子次序，其wavefN必須要變號。

但若兩個電子填在兩個不同軌域時,其total wavefN (spatial part times spin part)亦必須符合Pauling principle,例如 He*($1s^1 2p^1$) 其正確 total wavefN要如何寫?

先寫spatial part:

$$\Psi_{1s,2p}(1,2)=\frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{2p}(2)+\psi_{1s}(2)\psi_{2p}(1)) \quad \text{sym for exchange}$$

$$\Psi_{1s,2p}(1,2)=\frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{2p}(2)-\psi_{1s}(2)\psi_{2p}(1)) \quad \text{anti-sym for exchange}$$

Spin part:

$$\frac{1}{\sqrt{2}}(\alpha(1s)\beta(2p)-\beta(1s)\alpha(2p)) \quad \text{anti-sym}$$

$$\frac{1}{\sqrt{2}}(\alpha(1s)\beta(2p)+\beta(1s)\alpha(2p)) \quad \text{sym}$$

$$\alpha(1s)\alpha(2p) \quad \text{sym}$$

$$\beta(1s)\beta(2p) \quad \text{sym}$$

如何配才符合 Pauli principle?

Slater determinants

Slater suggested that there is a simple way to write wavefNs guaranteeing that they will be antisymmetric for interchange of electronic space and spin coordinates, for example 1s^{1}2s^1:

$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}}\{1s(1)\alpha(1)2s(2)\alpha(2) - 1s(2)\alpha(2)2s(1)\alpha(1)\}$$

$$= -\psi(2,1)$$

$$\text{try } 1\text{s}(1)\alpha(1)1\text{s}(2)\beta(2),\ \text{and } 1\text{s}^2 \text{ with two } \alpha \text{ electrons}$$

For three electrons wavefNs, $1s^2 2s^1$

$$\psi(1,2,3)=\frac{1}{\sqrt{3!}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) & 1s(3)\alpha(3) \\ 1s(1)\beta(1) & 1s(2)\beta(2) & 1s(3)\beta(3) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) & 2s(3)\alpha(3) \end{vmatrix}$$

$or,$

$$\psi(1,2,3)=\frac{1}{\sqrt{3!}}\begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ 1\bar{s}(1) & 1\bar{s}(2) & 1\bar{s}(3) \\ 2s(1) & 2s(2) & 2s(3) \end{vmatrix}$$

寫法為先以行的方式將各電子的 spin-orbitals寫上去,然後再填入電子的 indices,第一行填1,第二行填2,第三行填3。

展開後,任意交換兩電子,一定會變號, antisymmetric to the exchange of any two electron’s indices

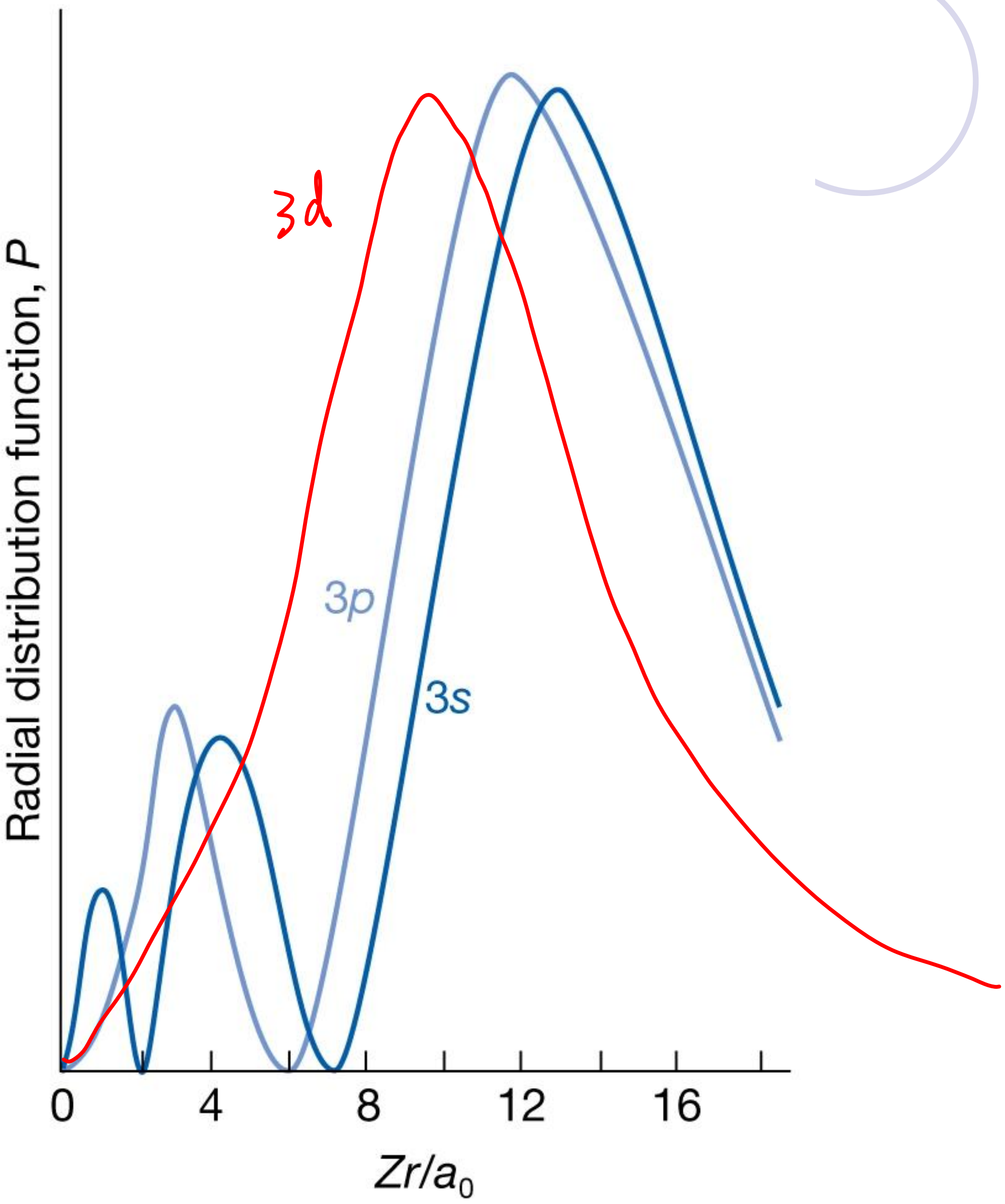
Penetration and shielding.

由radial distribution fN，可以解釋同一shell軌域中, S subshell 軌域比P subshell　軌域在靠近原子核附近有較大的電子分佈密度。$r_{m.p.}$

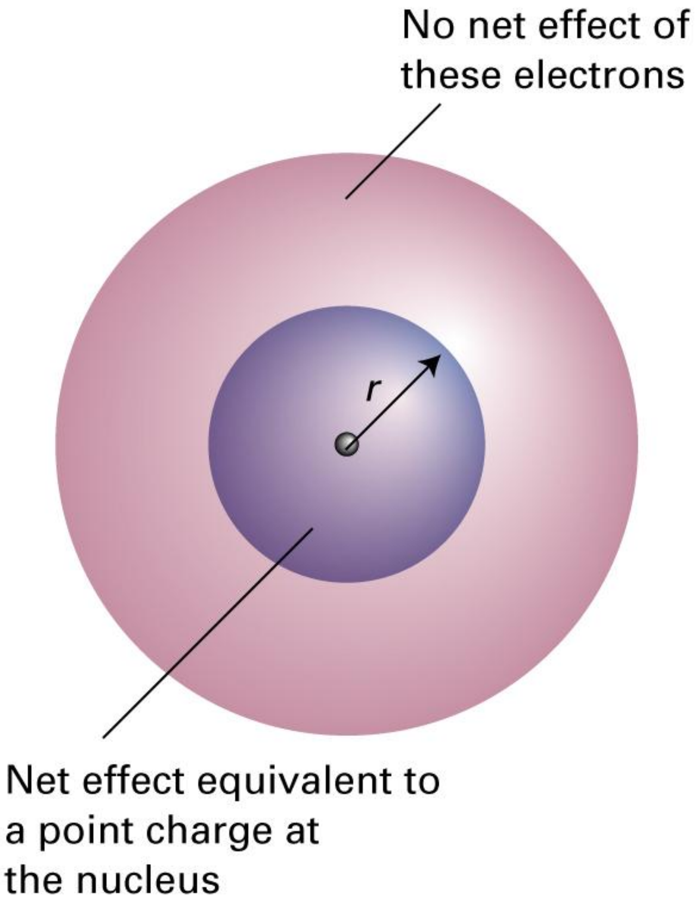
But, $<r>_s > <r>_p$

$$\boxed{<r>_{n,\ell} = n^2\left\{1+\frac{1}{2}\left(1-\frac{\ell(\ell+1)}{n^2}\right)\right\}\frac{a_\circ}{Z}}$$

參照Fig 9B.4, p374;因此S軌域的電子較不易被游離。這就說明不同subshell軌域的穿透(penetration)效應不同。ｄ軌域穿透比ｐ更小。在多電子原子中，在距離原子核較遠（外層）的電子，感受到核的吸引力，會受到內層電子排斥的影響而減弱。這種效應稱為shielding effect。其大小可視為所有內層電子聚集在原子核上，距離外層電子為ｒ所產生的斥力。



$\langle r \rangle > 0$,
$\langle r \rangle\uparrow$, $Z\downarrow$, $l\downarrow$, $n\uparrow$



在此層的電子沒有相互shielding effect ，但受到內層電子（假想聚集在中心核處形成一大負電粒子)的排斥距離為r，令其斥力為σ。

∴外層電子(valence electron)所受到的核吸引力扣除內層電子shielding 影響，$Z_{eff}= Z - \sigma$

因為s,p,d軌域的穿透效應不同，只能實驗結果來預估。

Refer to table 9.2 p345

The building–up (Aufbau) principle.

依據實驗結果所得到的中性原子的電子組態，設想出若一核帶有 z 個質子，外圍沒有電子，其電子填入軌域的順序：1s 2s 2p 3s 3p 4s 3d…..依據該principle所排出順序必須小心注意，尤其對能量接近的orbitals如4s, 3d, 常有複雜的$e^- \rightarrow e^-$ repulsion effects 而影響其順序。

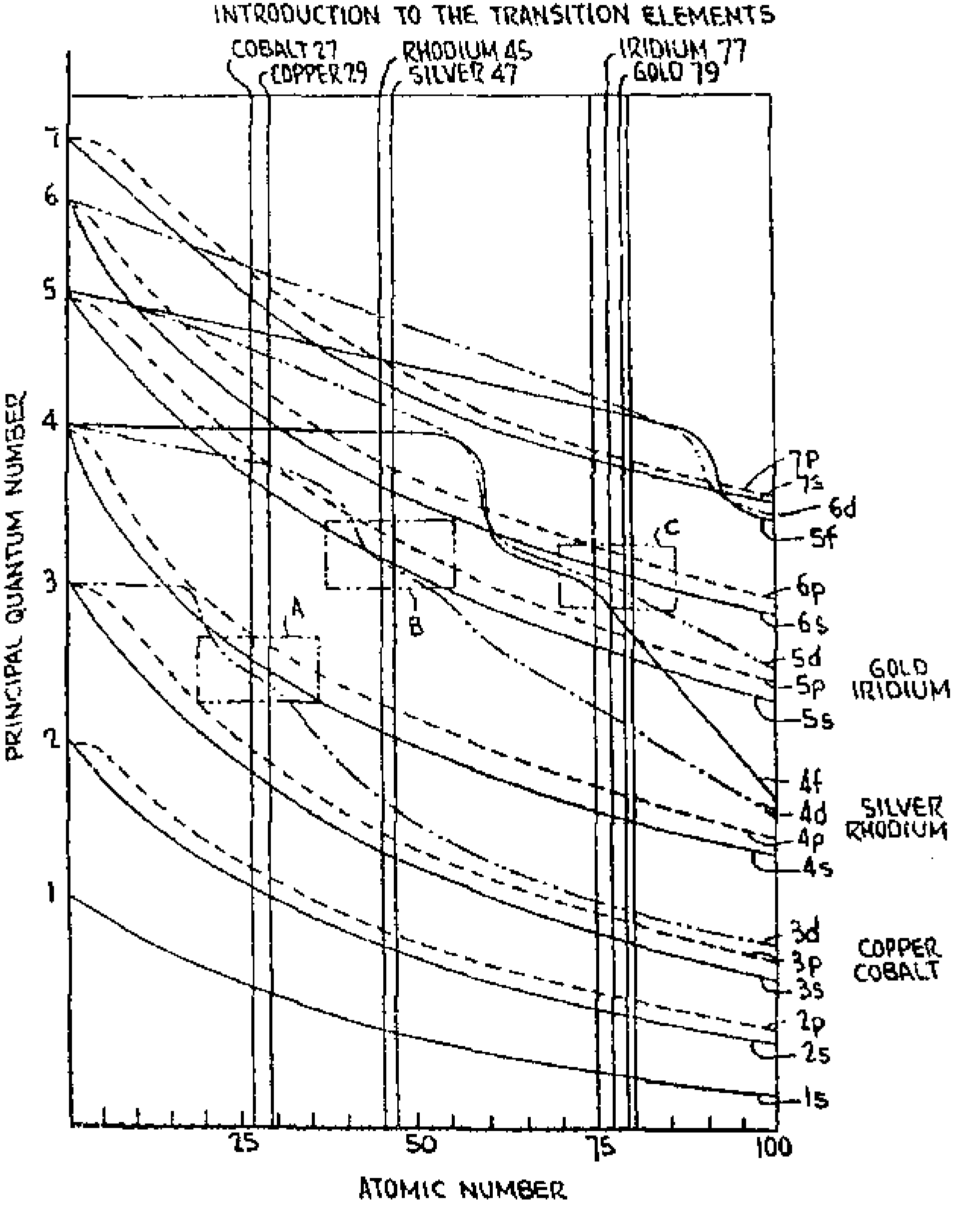
Electron configurations are determined either spectroscopically or by measurement of magnetic properties.

Hund’s maximum multiplicity rule:

An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.

1/10

FIG. 1



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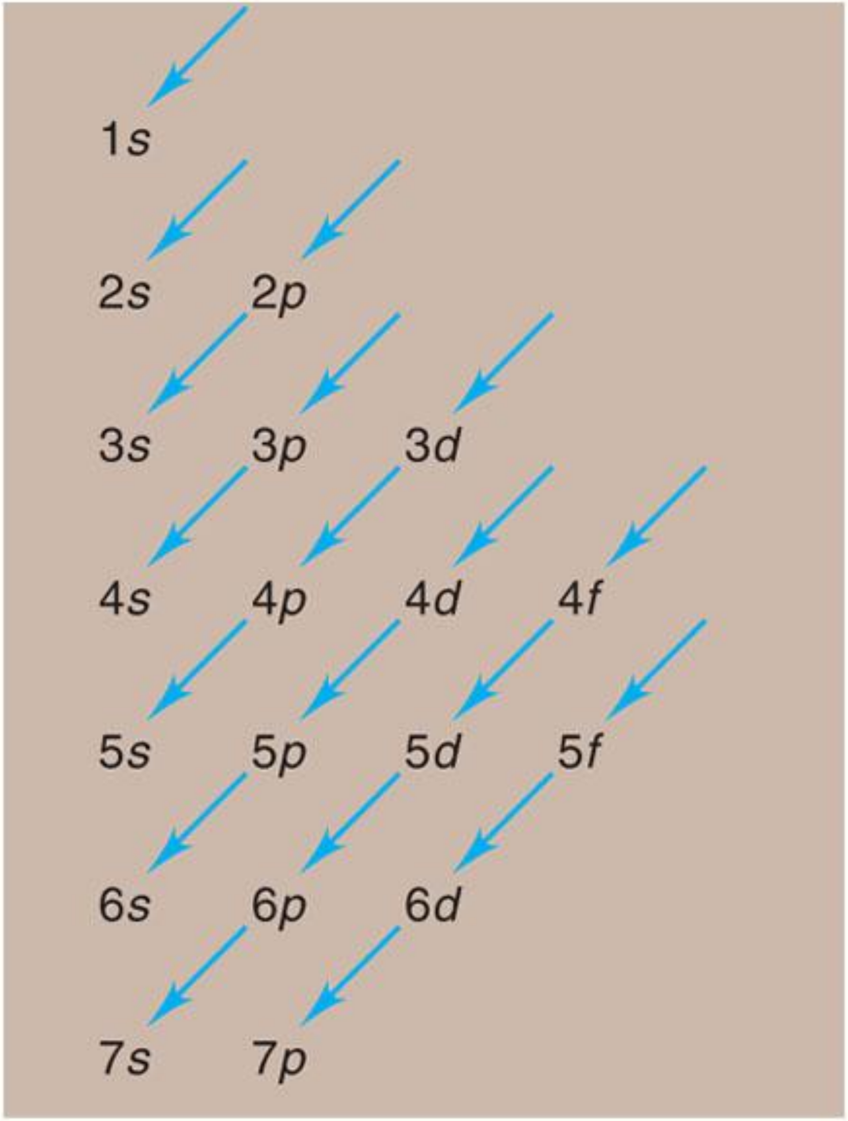
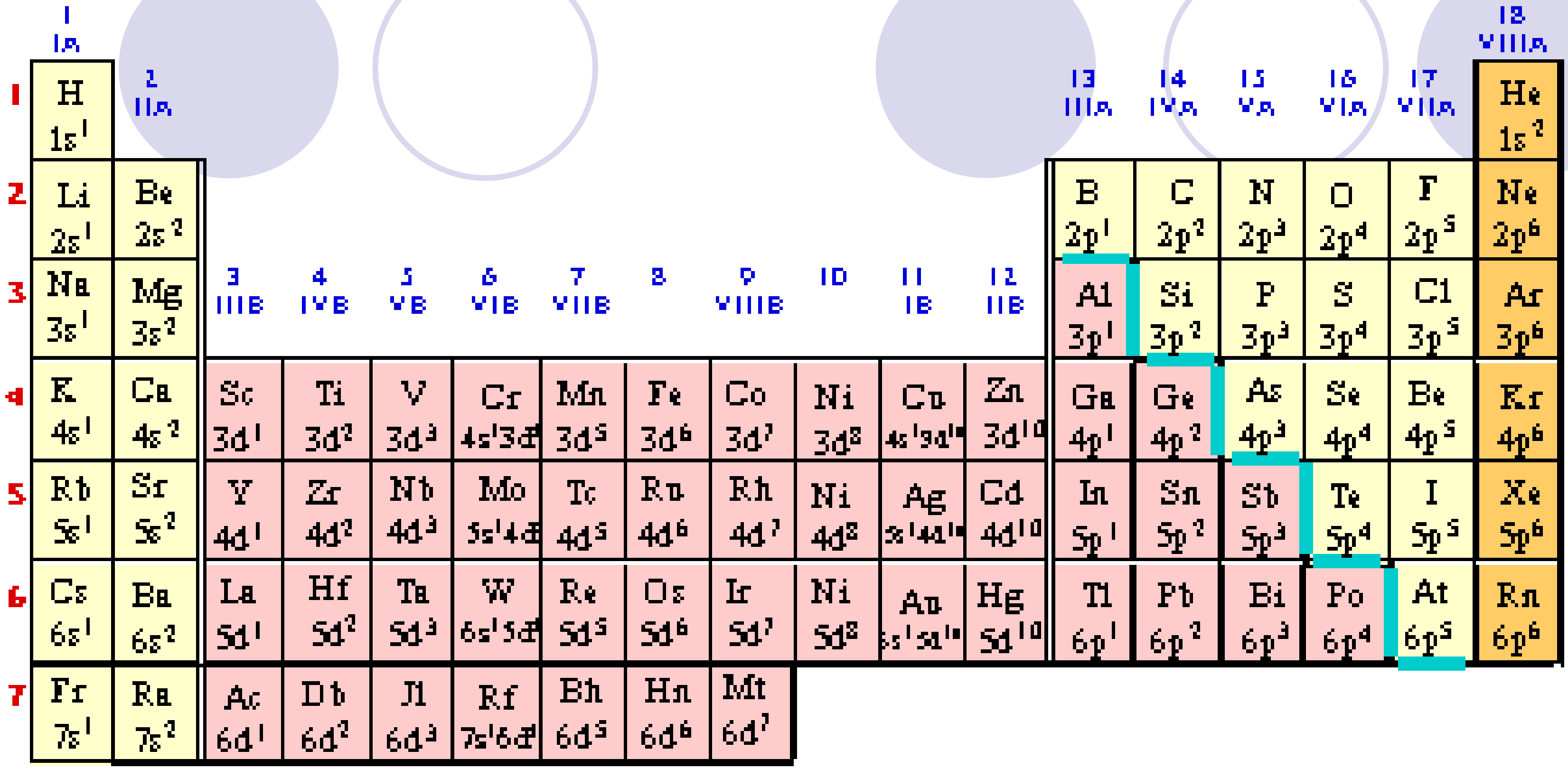




	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H $1s^1$																	He $1s^2$
2	Li $2s^1$	Be $2s^2$											B $2p^1$	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$	Ne $2p^6$
3	Na $3s^1$	Mg $3s^2$											Al $3p^1$	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$	Ar $3p^6$
4	K $4s^1$	Ca $4s^2$	Sc $3d^1$	Ti $3d^2$	V $3d^3$	Cr $4s^13d^5$	Mn $3d^5$	Fe $3d^6$	Co $3d^7$	Ni $3d^8$	Cu $4s^13d^{10}$	Zn $3d^{10}$	Ga $4p^1$	Ge $4p^2$	As $4p^3$	Se $4p^4$	Be $4p^5$	Kr $4p^6$
5	Rb $5s^1$	Sr $5s^2$	Y $4d^1$	Zr $4d^2$	Nb $4d^3$	Mo $5s^14d^5$	Tc $4d^5$	Ru $4d^6$	Rh $4d^7$	Ni $4d^8$	Ag $5s^14d^{10}$	Cd $4d^{10}$	In $5p^1$	Sn $5p^2$	Sb $5p^3$	Te $5p^4$	I $5p^5$	Xe $5p^6$
6	Cs $6s^1$	Ba $6s^2$	La $5d^1$	Hf $5d^2$	Ta $5d^3$	W $6s^15d^5$	Re $5d^5$	Os $5d^6$	Ir $5d^7$	Ni $5d^8$	Au $6s^15d^{10}$	Hg $5d^{10}$	Tl $6p^1$	Pb $6p^2$	Bi $6p^3$	Po $6p^4$	At $6p^5$	Rn $6p^6$
7	Fr $7s^1$	Ra $7s^2$	Ac $6d^1$	Db $6d^2$	Jl $6d^3$	Rf $7s^16d^5$	Bh $6d^5$	Hn $6d^6$	Mt $6d^7$									

e^- config. for Sulfur ?

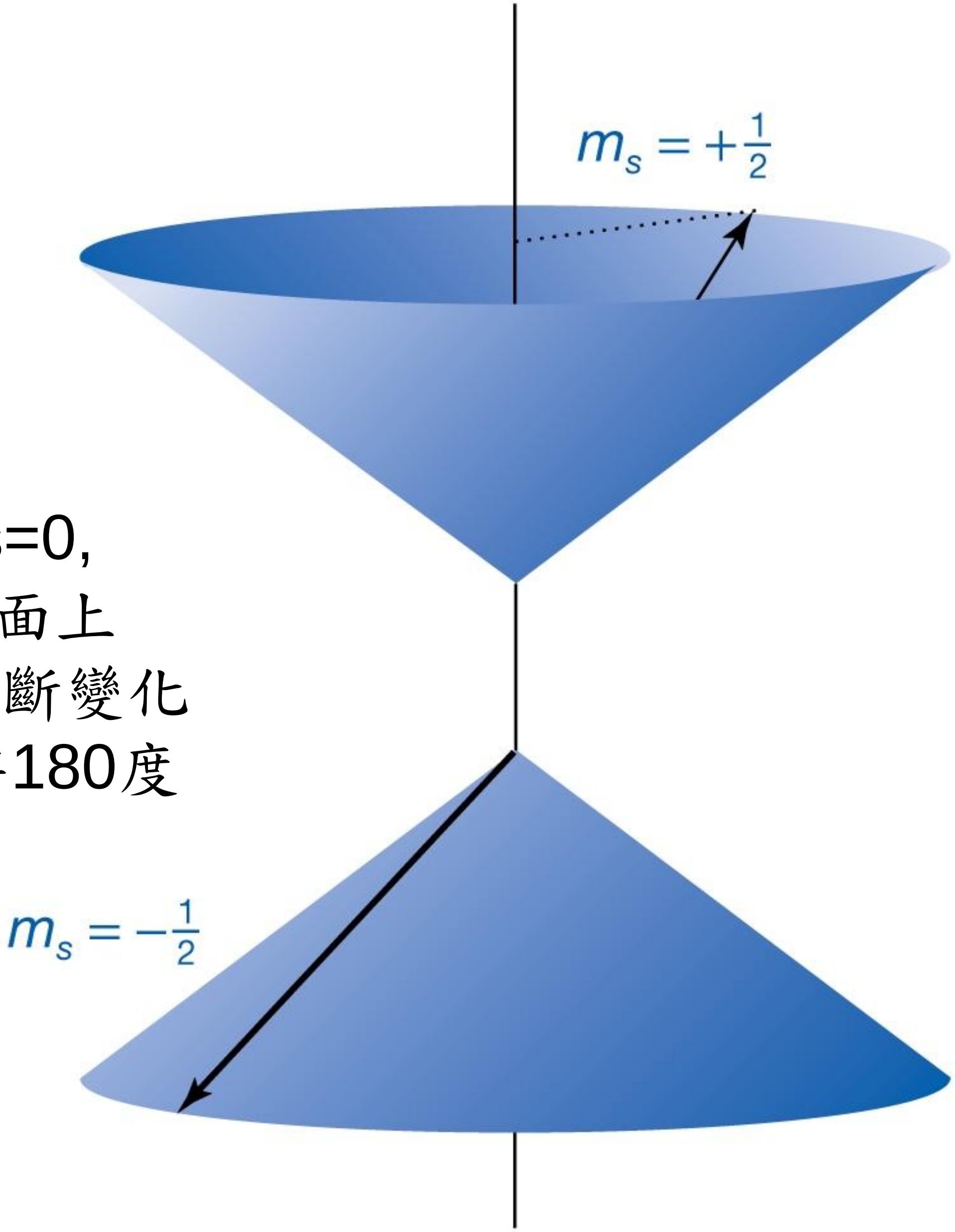
Singlet and triplet states

有兩個電子填入同一個 orbital 時，必須是 paired (↑↓) ，其total spin， S為0，則 2S+1=1，其中「 2S+1=1」 就稱為 spin-multiplicity 。

其值若為1 叫 singlet，若為2，叫「doublet」，若為3，叫「triplet」，4叫「quartet」…當然，若兩個電子填入不同orbitals時，就可能為singlet 或是 triplet 。

Electrons with paired spins have zero resultant spin angular momentum

- 他們的狀況可以如下圖所示
  two vectors lie at an undetermined position on the cones, but wherever one lies on its cone the other points in the opposite direction; their resultant is zero.



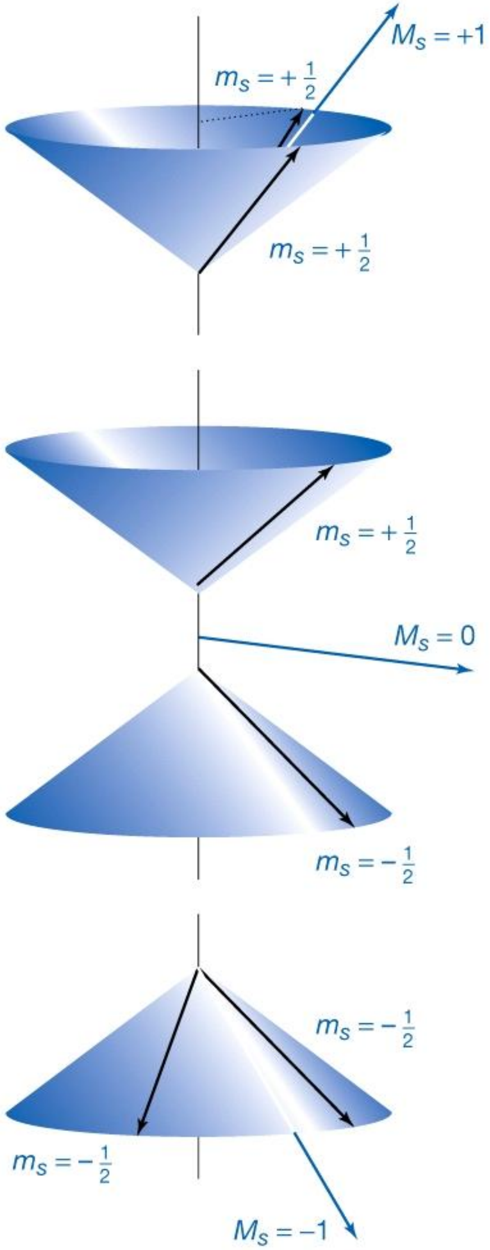
Paired spin, s=0,
M_s=0, 但xy平面上
的分量仍然不斷變化
兩者一直保持180度

This is called
Singlet.

Two electrons with parallel spins, have a nonzero total spin angular momentum. 有三種方式，其中 the angle between the vectors is the same in all three cases: the resultant of the two vectors have the same length in each case, but points in different directions.

This is called triplet

與前面paired spin 比較：
two paired spin are precisely antiparallel, however, two ‘parallel’ spins are not strictly parallel.



若最外層(shell) 只有一個電子時，一定是doublet？

依據Hund's rule，相同電子組態可以是singlet or triplet 時，以 triplet state 的能量較低。如He的excited state : $1s^1\ 2s^1$ 可以是singlet or triplet，但以 triplet state 能量較低，稱為該電子組態的**ground state**。

triplet的由來，是因該兩電子的m_s，可以是+1 / 2 or −1 / 2，其組合為1, 0, 0, −1四種狀態，其中三種是 symmetric to the exchange of electron label (triplet)，另一種是 anti-symmetric (singlet) 。

電子在做躍遷時，一般情況其spin是不變的
$\therefore$ triplet state $\rightarrow$ singlet state
是不予許的。

$$\left.\begin{array}{l}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}\end{array}\right\}\frac{\text{symmetric}}{(\text{triplet state})}$$

$$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}\quad\frac{\text{antisymmetric}}{(\text{singlet state})}$$

Total orbital angular momentum

- 在多電子原子系統 angular momentum 是一種向量加成一般利用Clebsch-Gordan series來處理，亦即(兩個,兩個加成)

$$\mathrm{L} = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots\ldots, |\ell_1 - \ell_2|$$

L : 稱 total angular momentum quantum number.

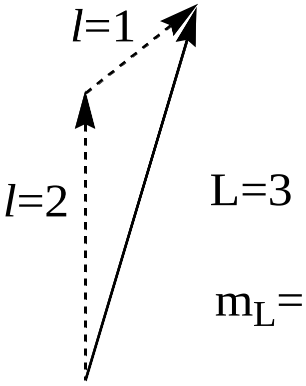
ℓ_1, ℓ_2 : 稱個別電子的angular momentum quantum number

而total angular momentum (magnitude)為 $\sqrt{\mathrm{L}(\mathrm{L}+1)}\hbar$ 或個別電子 orbital angular momentum (magnitude)為 $\sqrt{\ell(\ell+1)}\hbar$。

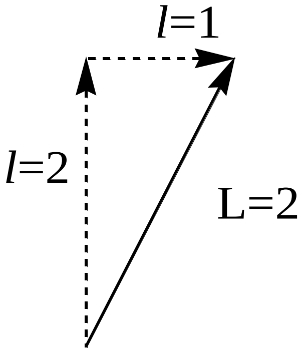
如 $\ell_1=2, \ell_2=1$ ，該兩者合成考慮方位（向量）先由L，得 L＝3，2，1 ，然而每個 L 又有 2L+1 個方位。

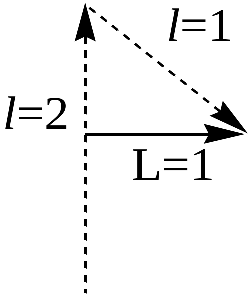
∴ 共有 7 + 5 + 3 = 15 個可能的結果，而這和 $\ell_1=2$（有5個方位），和 $\ell_2=1$（3個方位）的向量加成結果，應有 5 × 3 = 15 個結果是一致的。

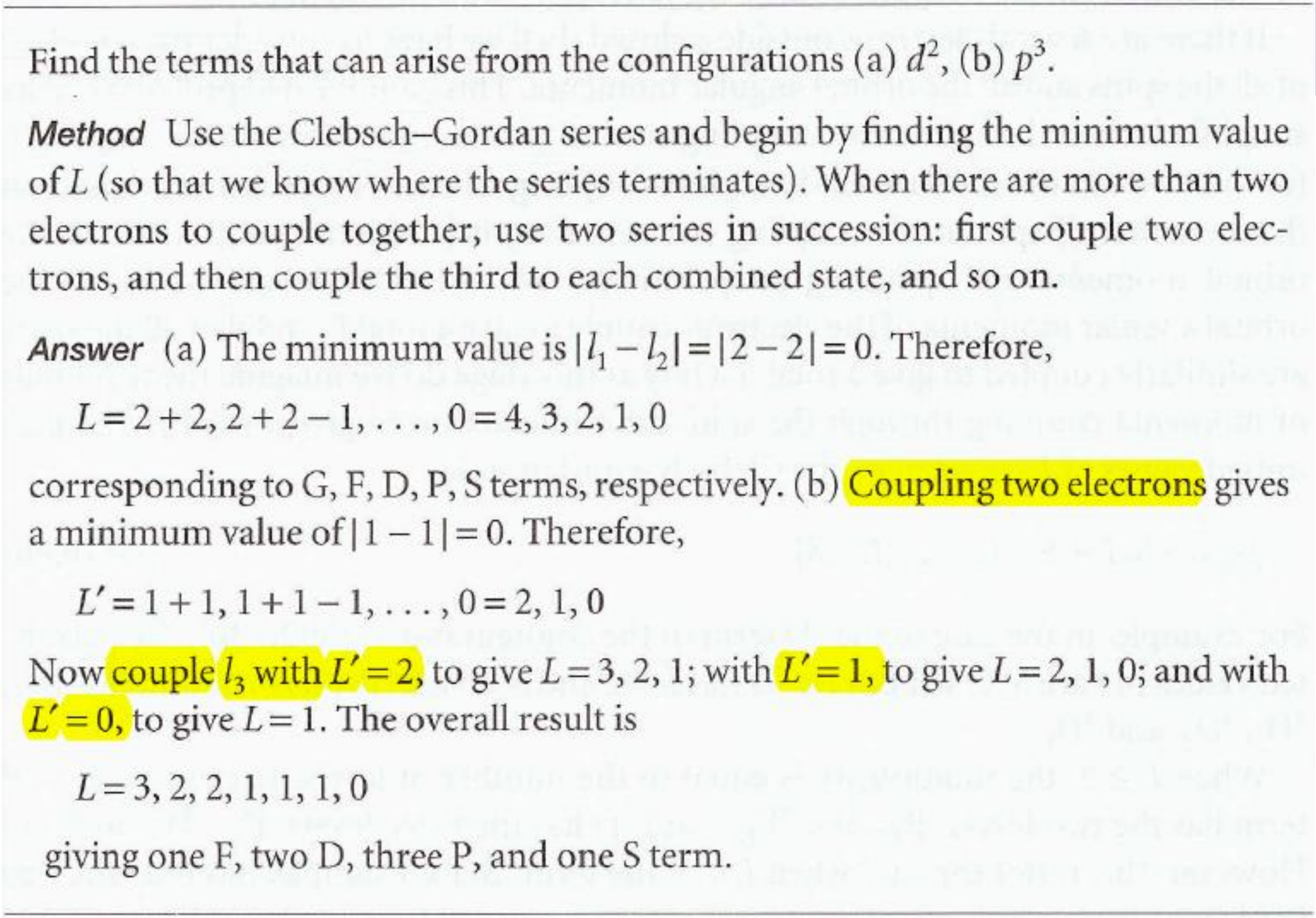
同理 $J = L+S, L+S-1, \ldots\ldots, |L-S|$，每個 J value 又有 2J+1 個方位，共應有 L×S 個加成方式，由此可見 Clebsh-Gordan series 的好用； 同理 $S = s_1+s_2, s_1+s_2-1, ..s_1-s_2$, for 2 electrons 共有 4 個可能的方位 (m_s)。



m_L= 3, 2, 1, 0, -1, -2, -3







Find the terms that can arise from the configurations (a) d^2, (b) p^3.

Method Use the Clebsch–Gordan series and begin by finding the minimum value of L (so that we know where the series terminates). When there are more than two electrons to couple together, use two series in succession: first couple two electrons, and then couple the third to each combined state, and so on.

Answer (a) The minimum value is $|l_1 - l_2| = |2 - 2| = 0$. Therefore,

$$L = 2 + 2, 2 + 2 - 1, \ldots, 0 = 4, 3, 2, 1, 0$$

corresponding to G, F, D, P, S terms, respectively. (b) Coupling two electrons gives a minimum value of $|1 - 1| = 0$. Therefore,

$$L' = 1 + 1, 1 + 1 - 1, \ldots, 0 = 2, 1, 0$$

Now couple l_3 with $L' = 2$, to give $L = 3, 2, 1$; with $L' = 1$, to give $L = 2, 1, 0$; and with $L' = 0$, to give $L = 1$. The overall result is

$$L = 3, 2, 2, 1, 1, 1, 0$$

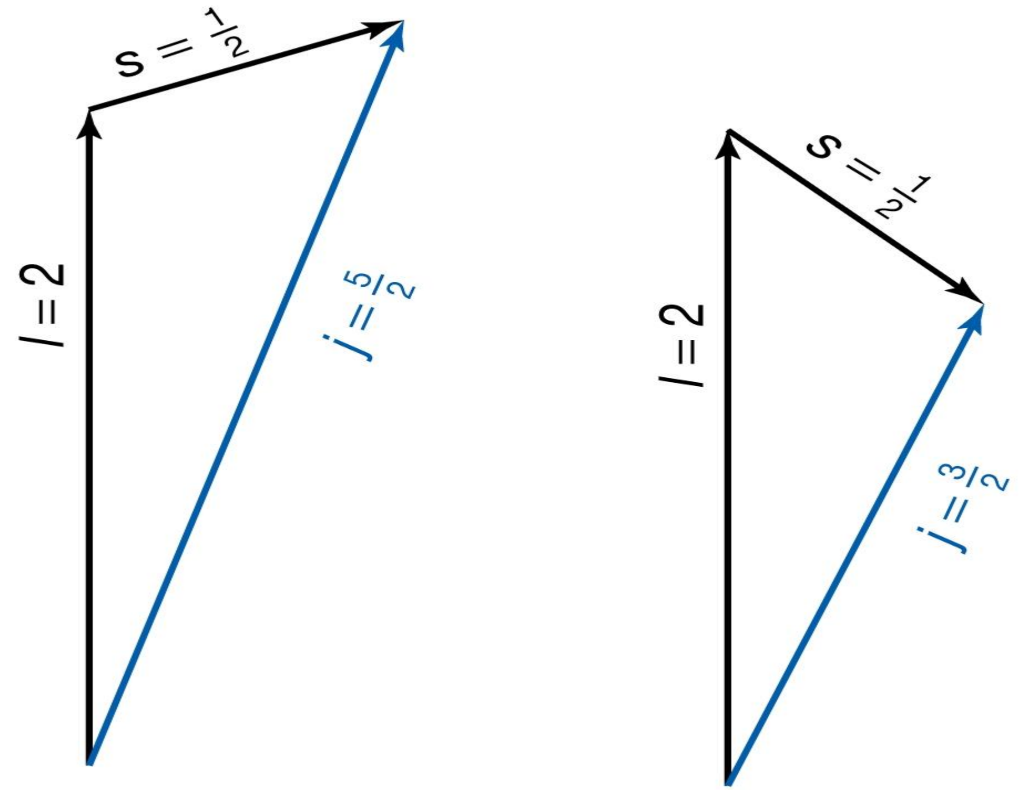
giving one F, two D, three P, and one S term.

Spin-orbit coupling

電子本身會 spin，產生magnetic moment，(spin magnetic moment)，其繞核運轉，產生orbital magnetic moment。

The interaction of the spin and orbital magnetic moments is called spin-orbit coupling，該interaction影響energy levels of the atom，depend on the relative orientation of the spin and orbital magnetic moments，其與spin angular momentum及orbital angular momentum的大小成正向，方位成反向關係。

(see fig 9.27 ，p354)



The coupling of the spin and orbital angular momenta of a d electron (l =2) gives two possible values of j. 依s and l 的相對orientation 而定

Russell – Saunders Coupling Scheme

LS coupling: many electrons, l, s → L, S → J

用於多電子的spin-orbit coupling is weak (light atoms)，因此把多個電子的 orbital momenta 一起合起來，再與多個電子合起來的spin momenta 相互作用

$$\therefore \quad L = \ell_1 + \ell_2 + \ldots\ldots \quad , \quad S = s_1 + s_2 + \ldots\ldots$$

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

Clebsch – Gordan series :描述兩個angular momentum向量加成的可能值，如：

ℓ_1 與 ℓ_2 其向量加成的可能值為 L

$$L = \ell_1 + \ell_2\,, \quad \ell_1 + \ell_2 - 1, \quad \ell_1 + \ell_2 - 2\,, \ldots\ldots, |\ell_1 - \ell_2|$$

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

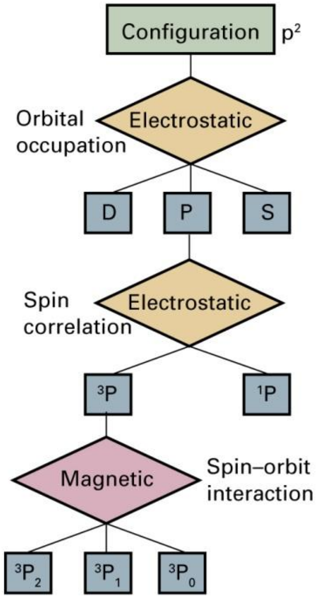
- Total angular momentum，$j=\ell+s,\quad \ell+s-1,\ldots\ldots,\ \ell-s$

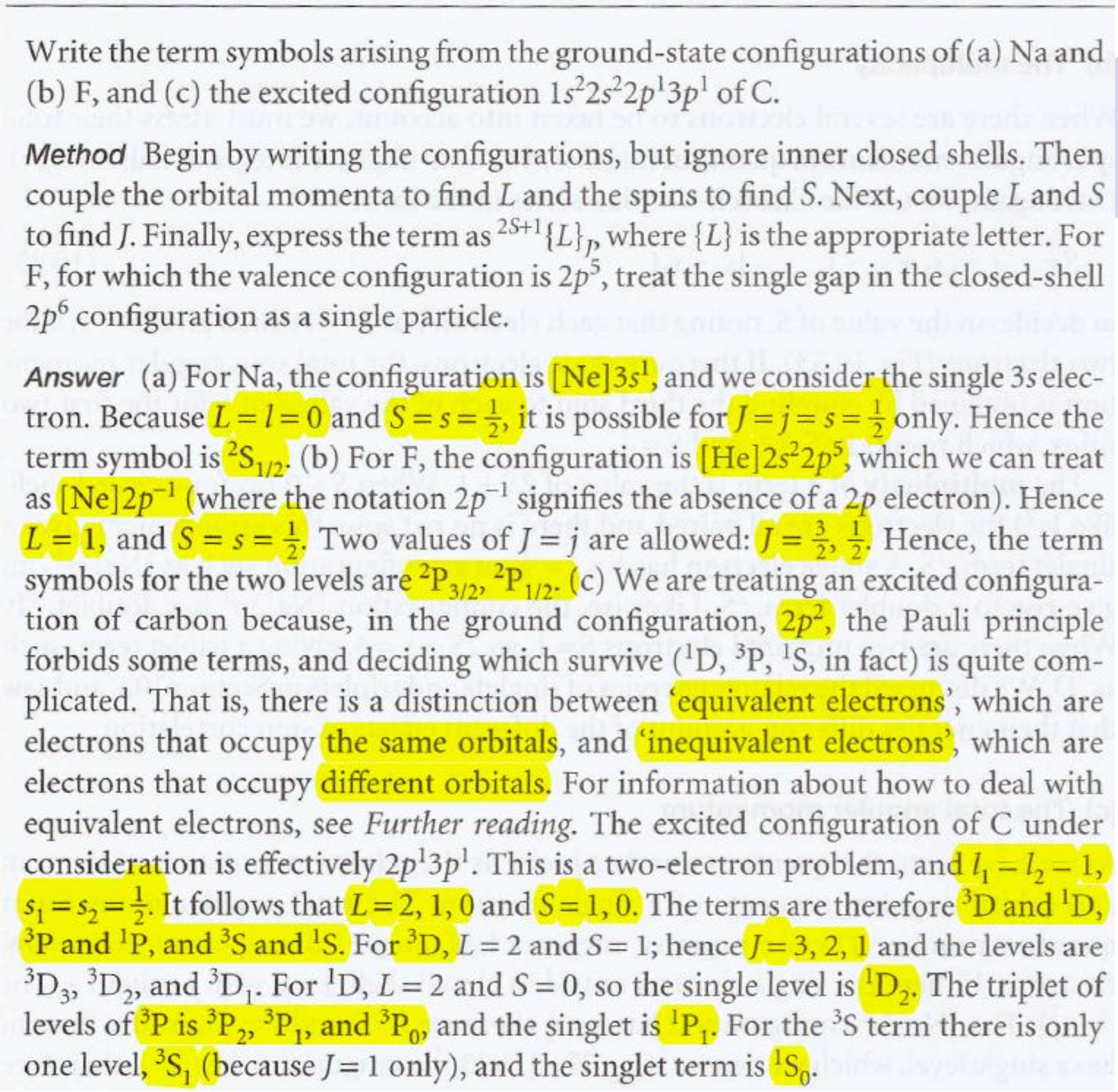
  eg. configuration為 d^1，其j=？ $\ell=2$，$s=\frac{1}{2}$，$j=\frac{5}{2}$，$\frac{3}{2}$

  p^1，其j=？ $\ell=1$，$s=\frac{1}{2}$，$j=\frac{3}{2}$，$\frac{1}{2}$

  f^1，其j=？ $\ell=3$，$s=\frac{1}{2}$，$j=\frac{7}{2}$，$\frac{5}{2}$

- Term Symbols $^{2s+1}L_J$ … L= 0，1，2，3， 4
  S，P，D，F，G

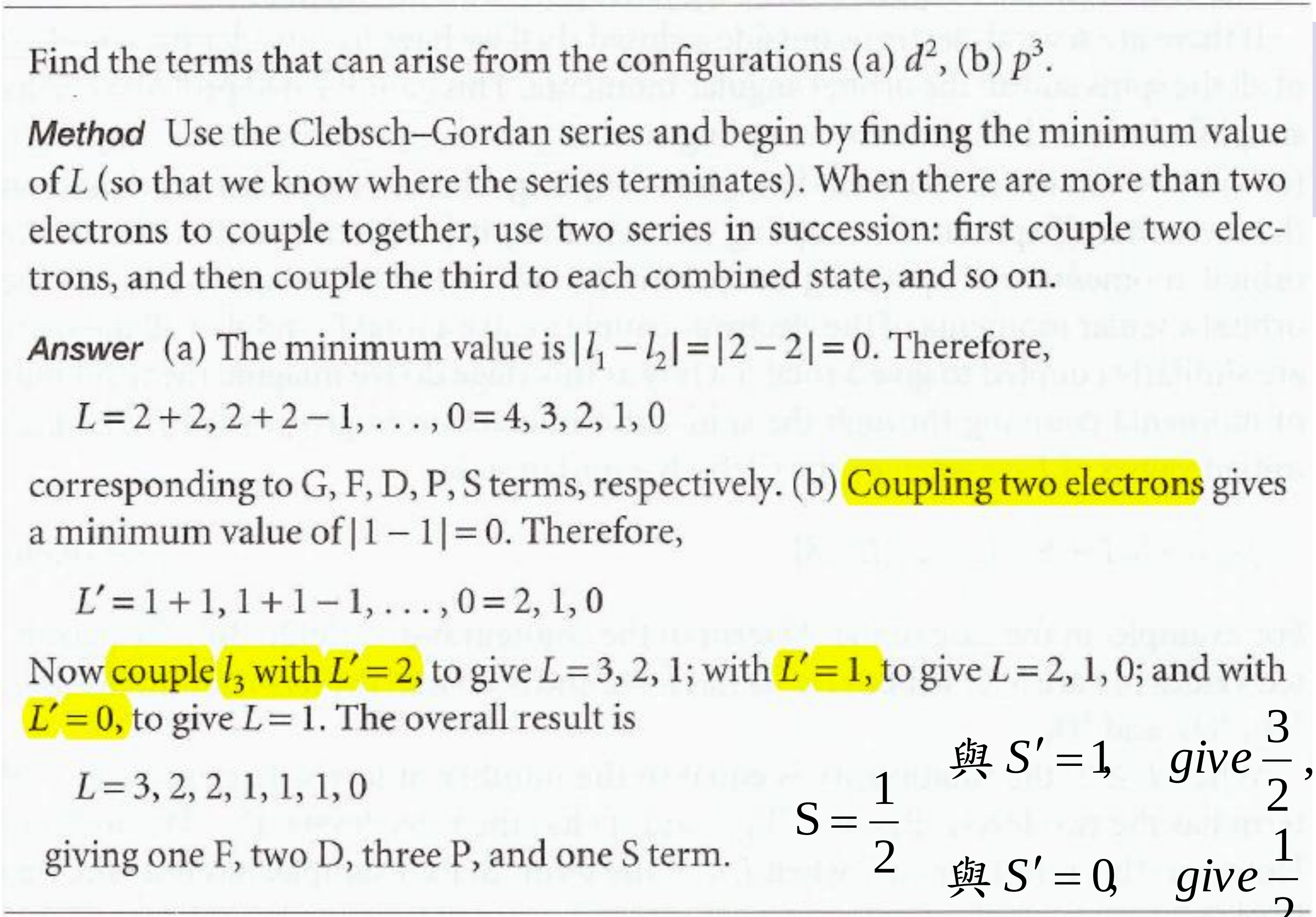




Write the term symbols arising from the ground-state configurations of (a) Na and (b) F, and (c) the excited configuration $1s^22s^22p^13p^1$ of C.

Method Begin by writing the configurations, but ignore inner closed shells. Then couple the orbital momenta to find L and the spins to find S. Next, couple L and S to find J. Finally, express the term as $^{2S+1}\{L\}_J$, where $\{L\}$ is the appropriate letter. For F, for which the valence configuration is $2p^5$, treat the single gap in the closed-shell $2p^6$ configuration as a single particle.

Answer (a) For Na, the configuration is $[\mathrm{Ne}]3s^1$, and we consider the single $3s$ electron. Because $L = l = 0$ and $S = s = \frac{1}{2}$, it is possible for $J = j = s = \frac{1}{2}$ only. Hence the term symbol is $^2\mathrm{S}_{1/2}$. (b) For F, the configuration is $[\mathrm{He}]2s^22p^5$, which we can treat as $[\mathrm{Ne}]2p^{-1}$ (where the notation $2p^{-1}$ signifies the absence of a $2p$ electron). Hence $L = 1$, and $S = s = \frac{1}{2}$. Two values of $J = j$ are allowed: $J = \frac{3}{2}, \frac{1}{2}$. Hence, the term symbols for the two levels are $^2\mathrm{P}_{3/2}$, $^2\mathrm{P}_{1/2}$. (c) We are treating an excited configuration of carbon because, in the ground configuration, $2p^2$, the Pauli principle forbids some terms, and deciding which survive ($^1\mathrm{D}$, $^3\mathrm{P}$, $^1\mathrm{S}$, in fact) is quite complicated. That is, there is a distinction between 'equivalent electrons', which are electrons that occupy the same orbitals, and 'inequivalent electrons', which are electrons that occupy different orbitals. For information about how to deal with equivalent electrons, see *Further reading*. The excited configuration of C under consideration is effectively $2p^13p^1$. This is a two-electron problem, and $l_1 = l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$. It follows that $L = 2, 1, 0$ and $S = 1, 0$. The terms are therefore $^3\mathrm{D}$ and $^1\mathrm{D}$, $^3\mathrm{P}$ and $^1\mathrm{P}$, and $^3\mathrm{S}$ and $^1\mathrm{S}$. For $^3\mathrm{D}$, $L = 2$ and $S = 1$; hence $J = 3, 2, 1$ and the levels are $^3\mathrm{D}_3$, $^3\mathrm{D}_2$, and $^3\mathrm{D}_1$. For $^1\mathrm{D}$, $L = 2$ and $S = 0$, so the single level is $^1\mathrm{D}_2$. The triplet of levels of $^3\mathrm{P}$ is $^3\mathrm{P}_2$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_0$, and the singlet is $^1\mathrm{P}_1$. For the $^3\mathrm{S}$ term there is only one level, $^3\mathrm{S}_1$ (because $J = 1$ only), and the singlet term is $^1\mathrm{S}_0$.



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$$L' = 1 + 1, 1 + 1 - 1, \ldots, 0 = 2, 1, 0$$

Now couple l_3 with $L' = 2$, to give $L = 3, 2, 1$; with $L' = 1$, to give $L = 2, 1, 0$; and with $L' = 0$, to give $L = 1$. The overall result is

$$L = 3, 2, 2, 1, 1, 1, 0$$

giving one F, two D, three P, and one S term.

$S = \frac{1}{2}$ 與 $S' = 1, \quad give\ \frac{3}{2}, \frac{1}{2}$

與 $S' = 0, \quad give\ \frac{1}{2}$

$\therefore \quad S = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$; $\quad 2S + 1 = 4$，2，2

∴可能的 *term symbols*： ${}^4F$, ${}^2F$, ${}^4D$, ${}^2D$, ${}^4P$, ${}^2P$, ${}^4S$, ${}^2S$

由 R-S coupling 求J

$${}^{4}F\,,\quad L=3.\quad S=\frac{3}{2}\quad \therefore J=\frac{9}{2},\frac{7}{2},\frac{5}{2},\frac{3}{2}\ \Rightarrow\ {}^{4}F_{9/2}\,,\ {}^{4}F_{7/2}\,,\ {}^{4}F_{5/2}\,,\ {}^{4}F_{3/2}$$

$${}^{2}F\,,\quad L=3.\quad S=\frac{1}{2}\quad \therefore J=\frac{7}{2}\,,\ \frac{5}{2}.\ \Rightarrow\ {}^{2}F_{7/2}\,,\ {}^{2}F_{5/2}$$

$${}^{4}D\,,\quad L=2.\quad S=\frac{3}{2}\quad \therefore J=\frac{7}{2},\frac{5}{2},\frac{3}{2},\frac{1}{2}\ \Rightarrow\ {}^{4}D_{7/2}\,,\ {}^{4}D_{5/2}\,,\ {}^{4}D_{3/2}\,,\ {}^{4}D_{1/2}$$

$${}^{2}D,\quad L=2\,,\quad S=\frac{1}{2}\quad \therefore\ J=\frac{5}{2}\,,\ \frac{3}{2}\ \Rightarrow\ {}^{2}D_{5/2}\,,\ {}^{2}D_{3/2}$$

$${}^{4}P,\quad L=1\,,\quad S=\frac{3}{2}\quad \therefore\ J=\frac{5}{2}\,,\ \frac{3}{2}\,,\ \frac{1}{2}\ \Rightarrow\ {}^{4}P_{5/2}\,,\ {}^{4}P_{3/2}\,,\ {}^{4}P_{1/2}$$

$${}^{2}P\,,\quad L=1\,,\quad S=\frac{1}{2}\quad \therefore J=\frac{3}{2},\frac{1}{2}\ \Rightarrow\ {}^{2}P_{3/2}\,,\ {}^{2}P_{1/2}$$

$${}^{4}S\,,\quad L=0\,,\quad S=\frac{3}{2}\quad \therefore\ J=\frac{3}{2}\ \Rightarrow\ {}^{4}S_{3/2}$$

$${}^{2}S\,,\quad L=0\,,\quad S=\frac{1}{2}\quad \therefore J=\frac{1}{2}\ \Rightarrow\ {}^{2}S_{1/2}$$

When *$L>S$, the multiplicity is equal to the number of levels*.

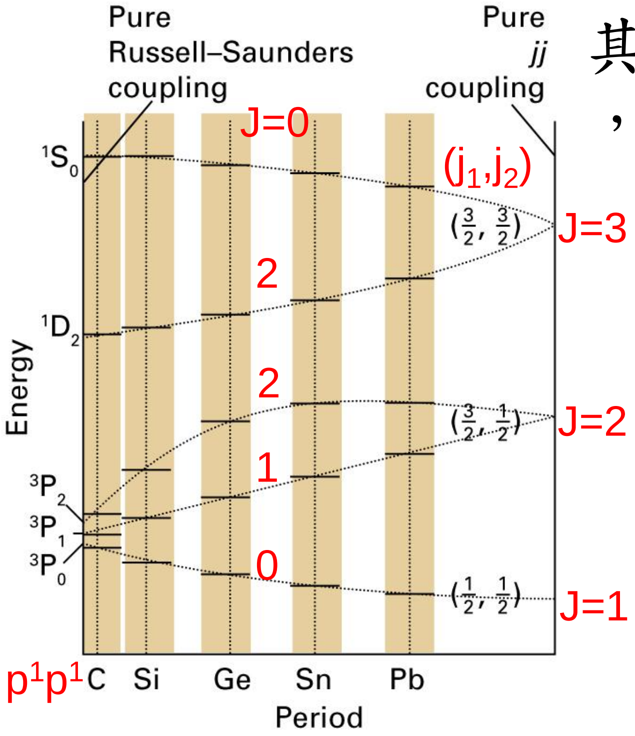
For example,${}^{2}p$ term has the two levels ${}^{2}p_{3/2}$and ${}^{2}p_{1/2}$‘

${}^{3}D$ has the three levels ${}^{3}D_{3}$,${}^{3}D_{2}$,and ${}^{3}D_{1}$

When *$L<S$: the term ${}^{2}S$, has only the one* level ${}^{2}S_{1/2}$'

LS coupling: many electrons, l, s → j and jj→J

如果是heavy atom時，R-S coupling不適用，必須用 *j-j* coupling。每一個電子只考慮total angular momentum (spin, orbit加成) j，每個電子再與每個電子的相互作用，此時的 $L=\ell_1+\ell_2+\ldots..$， $S=s_1+s_2+\ldots$ 就相對不太重要了。如 P^2 組態 $\ell_1=1,\ \ell_2=1;\quad s_1=\frac{1}{2},\ s_2=\frac{1}{2}$



其每個電子的可能total angular momentum為，彼此互相coupling的情況為：j= $\frac{3}{2}$ or $\frac{1}{2}$

$$\left.\begin{array}{ll} j_1=\frac{3}{2} \quad j_2=\frac{3}{2} & \Rightarrow\ J=3,\ 2,\ 1,\ 0 \\ j_1=\frac{3}{2} \quad j_2=\frac{1}{2} & \Rightarrow\ J=2,1 \\ j_1=\frac{1}{2} \quad j_2=\frac{3}{2} & \Rightarrow\ J=2,1 \\ j_1=\frac{1}{2} \quad j_2=\frac{1}{2} & \Rightarrow\ J=1,0 \end{array}\right\}$$

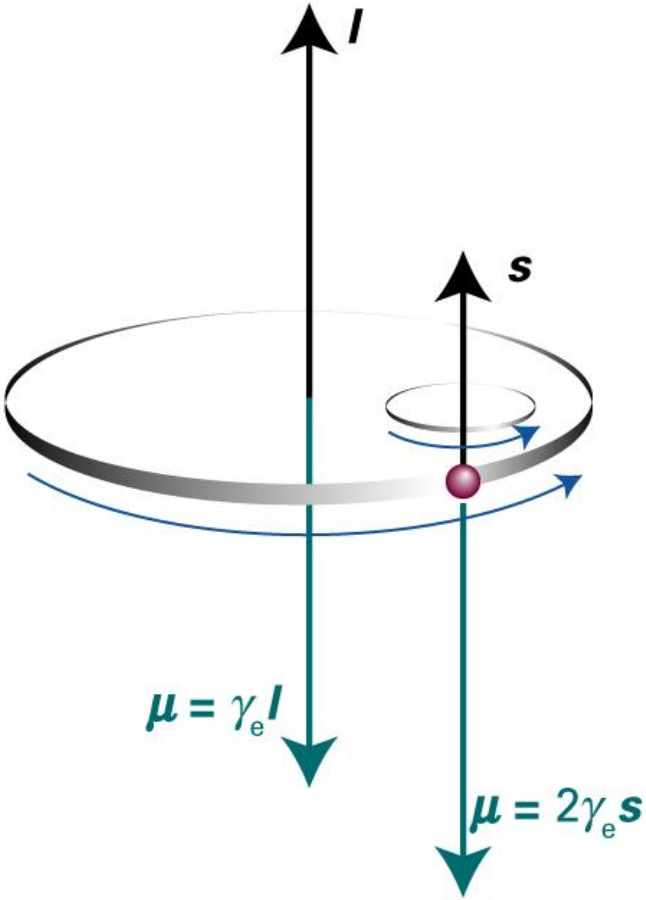
基本上，重原子以 J 為較可信的quantum number.

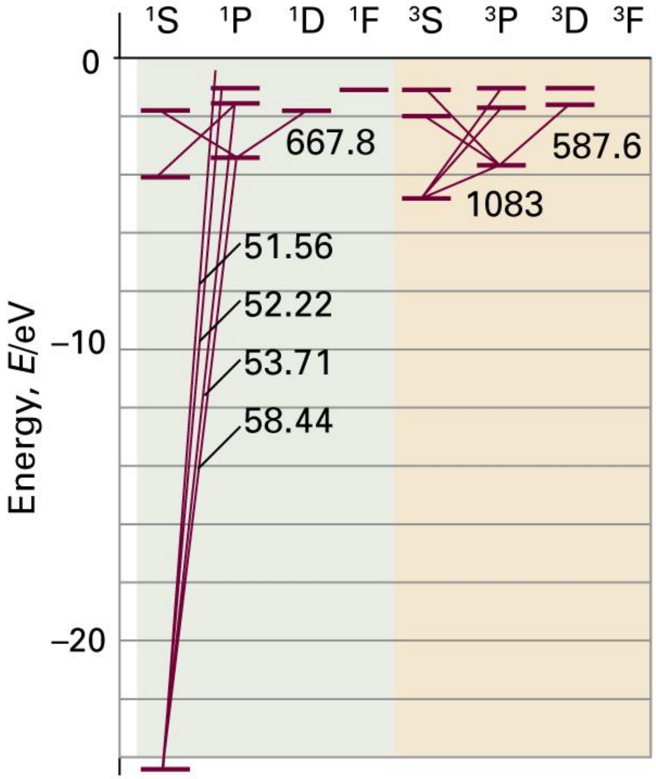
如圖所示，原子越大，其能階正確值越趨近於由 $j-j$ 所計算的結果。

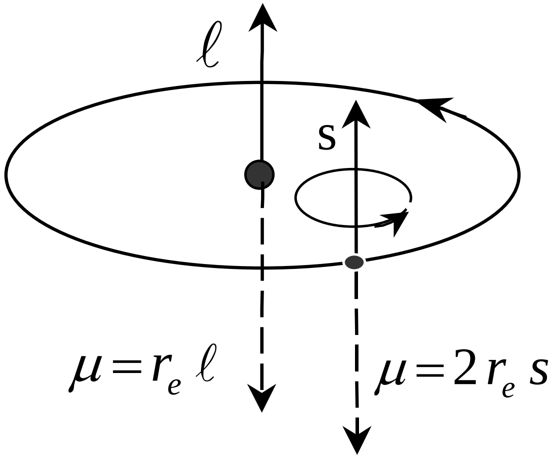
R-S 在heavy atom 雖然不適，但其推演出來的 term symbol 仍然有效，因為其能階的順序仍然沒變，雖然能階差有明顯變化。

Angular momentum gives rise to a magnetic moment (μ). 其與angular momentum 大小乘正比但方向相反

For spin angular momentum there is a factor 2, which increases the magnetic moment to twice its expected value.







其中 r_e 稱為 magnetogyric ratio，$r_e = \frac{-e}{2m_e}$

如果e^- 的orbital angular momentum為 $\vec{L}$

$$\left|\vec{L}\right| = \sqrt{\ell(\ell+1)}\ \hbar$$ ，則其在z軸

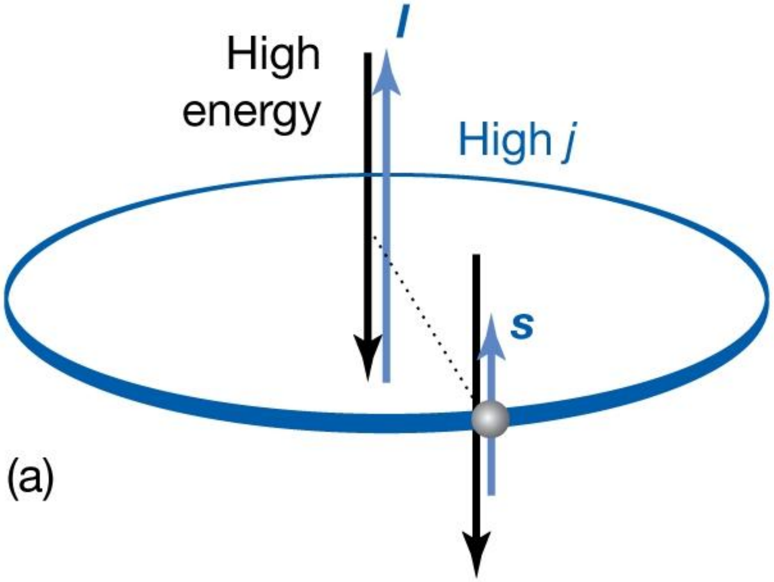
的分量 $L_Z = m_L \hbar$

則 $$\mu_Z = r_e m_L \hbar = -\frac{e\hbar}{2m_e} m_L = -\mu_\beta m_L$$

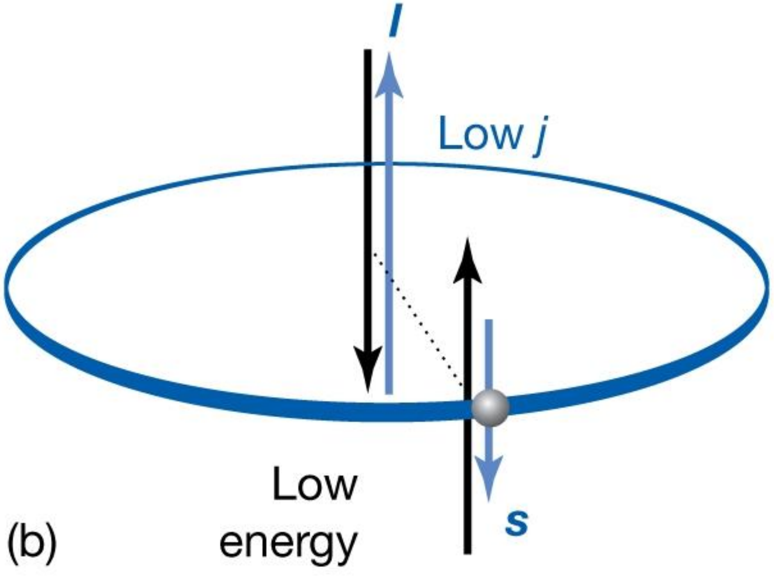
$$\underline{\underline{\mu_\beta = \frac{e\hbar}{2m_e}}}$$ … 稱 Bohr magneton

$\mu_\beta = 9.274 \times 10^{-24}$ JT^{-1}… fundamental quantum of magnetic moment.

The two angular momentum are parallel and the magnetic moment are aligned unfavorably. 相斥



The two angular momentum are antiparallel and the magnetic moment are aligned favorably, 相吸



The interaction energy of a magnetic moment, μ, in a magnetic field, B, is: $E=-\mu\cdot B$, 為一 scalar product。所以假設電子的orbital angular momentum 所產生的 magnetic field 與s 相互作用能量 E, 應正比於 $s\cdot\ell$

如何求$s\cdot\ell$?

令 $\vec{j} = \vec{\ell} + \vec{s}$?

則 $\vec{j} \cdot \vec{j} = (\ell + s) \cdot (\ell + s) = \vec{\ell} \cdot \vec{\ell} + \vec{s} \cdot \vec{s} + \boxed{2\vec{\ell} \cdot \vec{s}}$

$$\left.\begin{array}{lll} \vec{\ell} \cdot \vec{\ell} & \propto & \ell(\ell+1) \\ \vec{j} \cdot \vec{j} & \propto & j(j+1) \\ \vec{s} \cdot \vec{s} & \propto & s(s+1) \end{array}\right\} \text{代入}$$

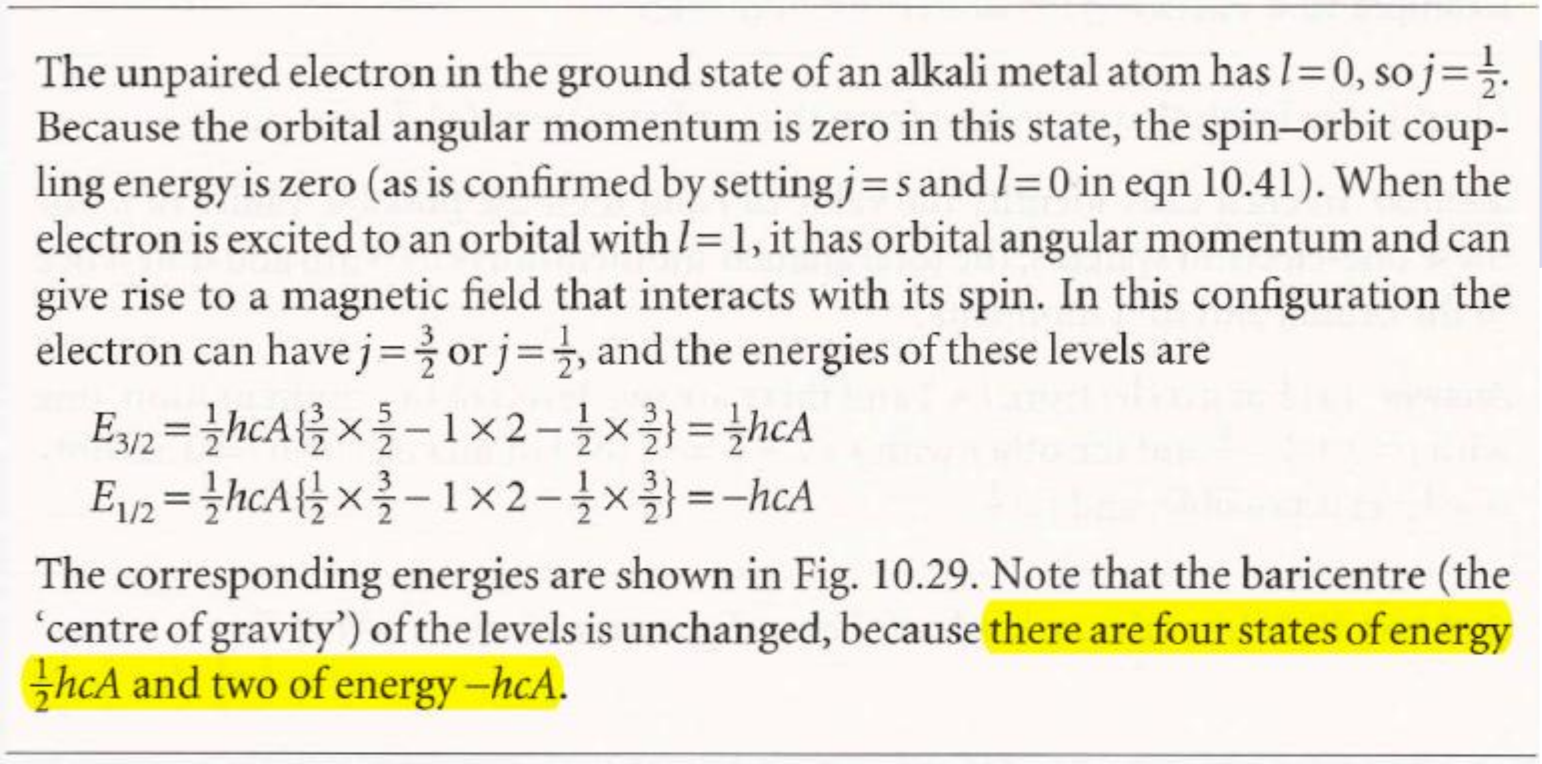
$$\therefore \; s \cdot \ell \; \propto \; j(j+1) - \ell(\ell+1) - s(s+1)$$

$$\therefore \; E \; \propto \; j(j+1) - \ell(\ell+1) - s(s+1)$$

$$E_{j,\ell,s} = \frac{1}{2} hcA \{ j(j+1) - \ell(\ell+1) - s(s+1) \}$$

*A*稱為 spin-orbit coupling constant for particular atom

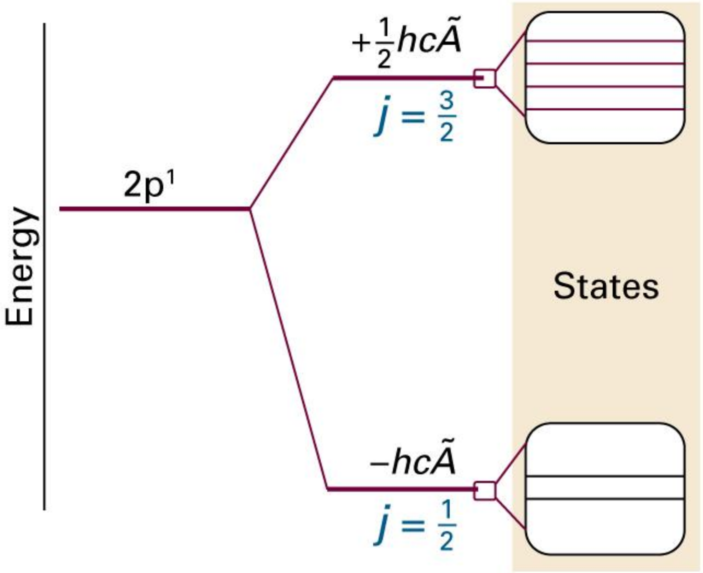
ls coupling: one electron, small j, l, s



The unpaired electron in the ground state of an alkali metal atom has $l=0$, so $j=\frac{1}{2}$. Because the orbital angular momentum is zero in this state, the spin–orbit coupling energy is zero (as is confirmed by setting $j=s$ and $l=0$ in eqn 10.41). When the electron is excited to an orbital with $l=1$, it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. In this configuration the electron can have $j=\frac{3}{2}$ or $j=\frac{1}{2}$, and the energies of these levels are

$$E_{3/2}=\tfrac{1}{2}hcA\{\tfrac{3}{2}\times\tfrac{5}{2}-1\times 2-\tfrac{1}{2}\times\tfrac{3}{2}\}=\tfrac{1}{2}hcA$$
$$E_{1/2}=\tfrac{1}{2}hcA\{\tfrac{1}{2}\times\tfrac{3}{2}-1\times 2-\tfrac{1}{2}\times\tfrac{3}{2}\}=-hcA$$

The corresponding energies are shown in Fig. 10.29. Note that the baricentre (the 'centre of gravity') of the levels is unchanged, because there are four states of energy $\frac{1}{2}hcA$ and two of energy $-hcA$.

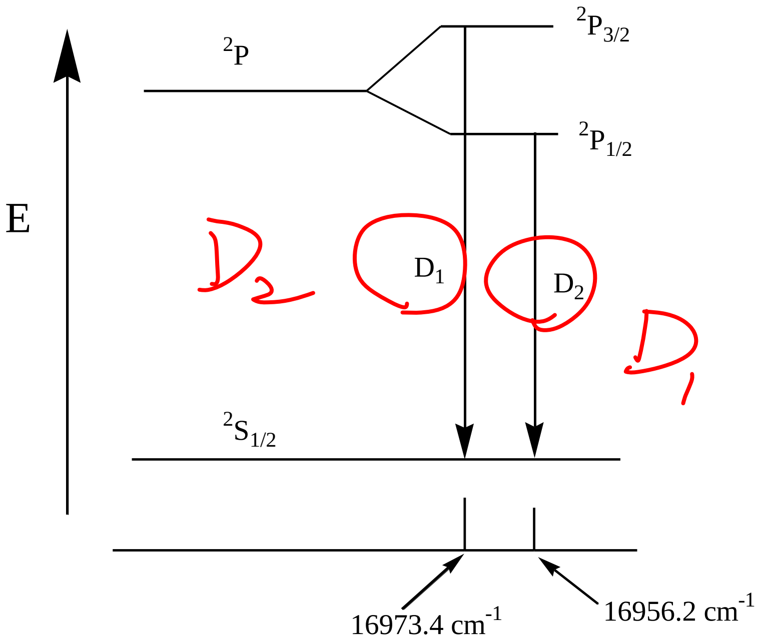


如 Na atom 基態電子組態為 $[Ne]3s^1$，其excited state為 $[Ne]3p^1$ 則excited state的total angular momentum有幾種值？

$j=\ell+s,\ \ell+s-1,\ldots\ldots,\ \ell-s$ $\because \ell=1,\ s=\frac{1}{2}$ $\therefore\ j=\frac{3}{2},\frac{1}{2}$ 有兩種

而ground state $j=\frac{1}{2}$ 寫成 term symbol形式 $^{2s+1}L_j$，excited state有兩項 $^2P_{3/2}$，$^2P_{1/2}$，ground state只有一項 $^2S_{1/2}$。

由於 excited state 的 spin-orbit coupling 使 excited state 能階split 成 two levels。



由Sodium D line splitting 可求出 Na 的spin-orbit coupling constant “A”.

$$E_{j,\ell,s} = E_{3/2,1,1/2} = \frac{1}{2}hcA\left\{\frac{3}{2}\left(\frac{3}{2}+1\right)-\ell(\ell+1)-s(s+1)\right\}$$

$$E_{1/2,1,1/2} = \frac{1}{2}hcA\left\{\frac{1}{2}\left(\frac{1}{2}+1\right)-\ell(\ell+1)-s(s+1)\right\}$$

$$\frac{\Delta E}{hc} = \frac{E_{3/2,1,1/2}-E_{1/2,1,1/2}}{hc} = \mathrm{D}_2 \text{ line and } \mathrm{D}_1 \text{ line 的間距}$$

$$=\frac{1}{2}A\left\{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)\right\}=\frac{3}{2}A=(16973.4-16956.2)cm^{-1}=17.2\,cm^{-1}$$

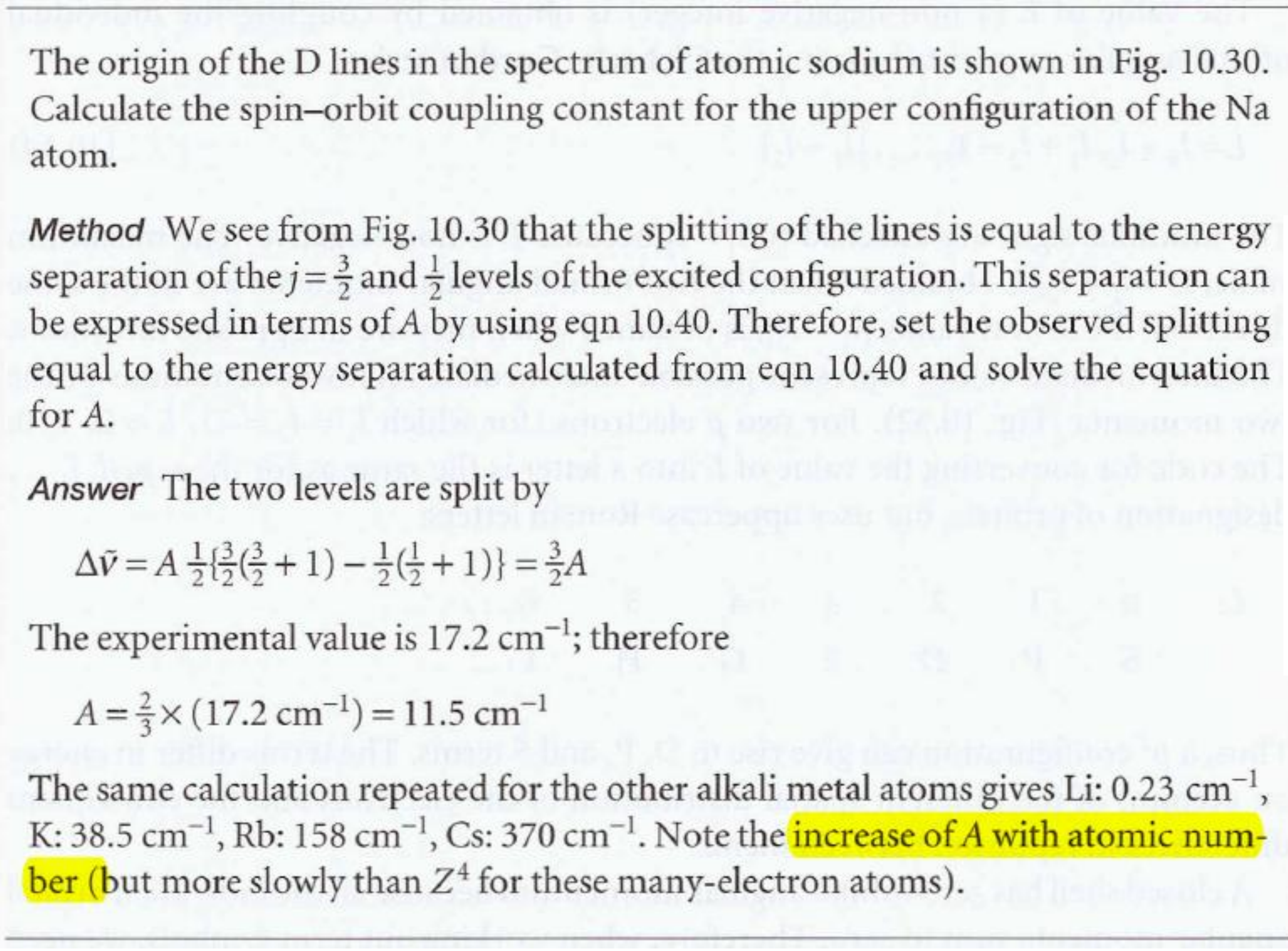
$$\therefore \quad A = 17.2\ cm^{-1} \times \frac{2}{3} = 11.5\ \ cm^{-1}$$

類似的問題應用於Alkali metal (Li，K， Rb，Cs)的 D line splitting , 如：

$$Li: 0.23\,cm^{-1}，\ K: 38.5\,cm^{-1}，Rb: 158\,cm^{-1}，\ Cs: 370\,cm^{-1}$$

可見spin-orbit coupling constant隨原子增大而增加，表示spin-orbit interaction在 heavy atom中是相當大的，也相當重要。

Fine Structure of a spectrum, the structure in a spectrum due to spin-orbit coupling.



The origin of the D lines in the spectrum of atomic sodium is shown in Fig. 10.30. Calculate the spin–orbit coupling constant for the upper configuration of the Na atom.

Method We see from Fig. 10.30 that the splitting of the lines is equal to the energy separation of the $j=\frac{3}{2}$ and $\frac{1}{2}$ levels of the excited configuration. This separation can be expressed in terms of A by using eqn 10.40. Therefore, set the observed splitting equal to the energy separation calculated from eqn 10.40 and solve the equation for A.

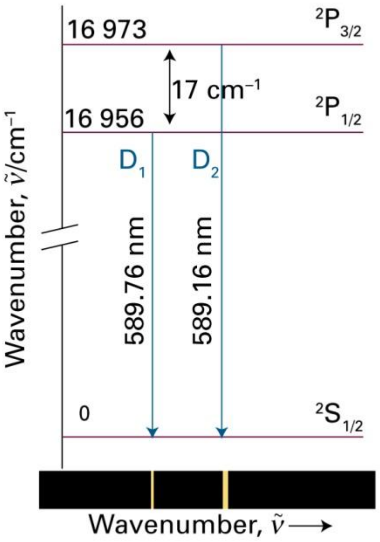
Answer The two levels are split by

$$\Delta\tilde{\nu} = A\,\tfrac{1}{2}\{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)\} = \tfrac{3}{2}A$$

The experimental value is 17.2 cm^{-1}; therefore

$$A = \tfrac{2}{3}\times(17.2\ \mathrm{cm}^{-1}) = 11.5\ \mathrm{cm}^{-1}$$

The same calculation repeated for the other alkali metal atoms gives Li: 0.23 cm^{-1}, K: 38.5 cm^{-1}, Rb: 158 cm^{-1}, Cs: 370 cm^{-1}. Note the increase of A with atomic number (but more slowly than Z^4 for these many-electron atoms).



Selection rule：

基於photon的spin angular momentum為+1

$$\Delta S = 0, \quad \Delta L = 0, \pm 1, \; (\Delta \ell = \pm 1)$$

$$\Delta J = 0, \pm 1, \; (\text{but} \;\; J = 0 \not\longleftrightarrow J = 0)$$

$$^2P_{3/2} \xrightarrow{emission} {}^2S_{1/2} \qquad {}^2P_{1/2} \xrightarrow{emission} {}^2S_{1/2}$$

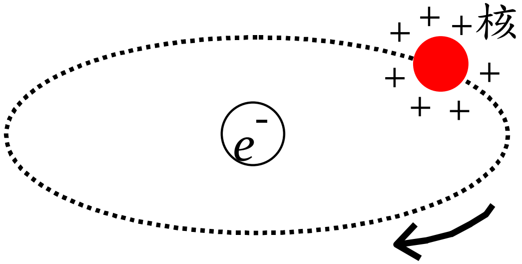
$$^2P_{3/2} \xleftarrow[absorption]{} {}^2S_{1/2} \qquad {}^2P_{1/2} \xleftarrow[absorption]{} {}^2S_{1/2}$$

一般習慣寫法，能量高的term寫在前面，能量低的term寫在後面，用 → *or* ← 表示 *emission or absorption*

這裡有一很重要的法則必須遵守的是ΔS=0，亦即singlet ↔ singlet；doublet↔ doublet；triplet↔ triplet
不可跨越。但對heavy atoms而言，因為L, S的 quantum number已不那麼適用，取而代之的是J quantum number，因此ΔS=0 的法則在heavy atom的transition就沒有那麼嚴格遵守，而常有multiplicity跨越的transition。

重原子的 spin – orbit coupling 為什麼重要?

電子繞核運動，若對電子而言(站在電子上)如同核繞電子而轉，核電荷繞轉會在電子上產生一磁通量，與該電子的spin magnetic moment 相互作用，而磁通量的大小與該核電荷成正比，因此 heavy atom，其 spin – orbit coupling是相當顯著的。

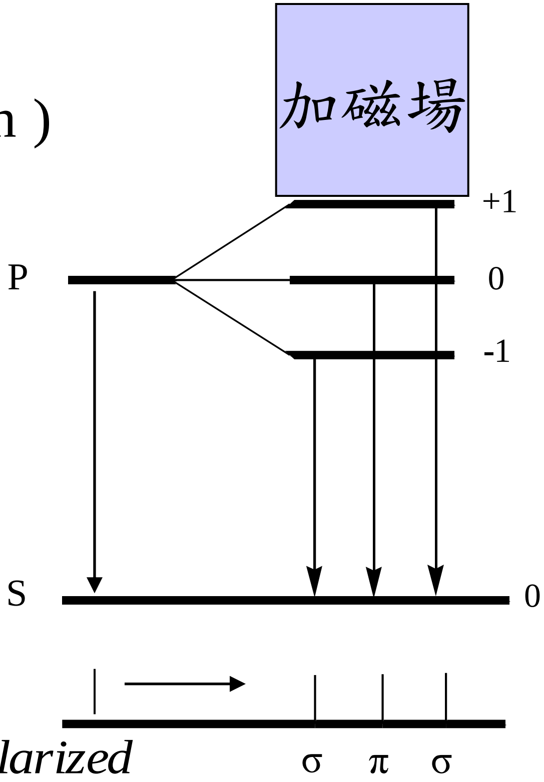


Zeeman effect

電子繞軌域運轉所產生的magnetic moment 在外加磁場的作用下, 產生不同作用能使原本的單一能階分裂成多條，其譜線由一條變成多條。

作用能 $E = -\mu_z B = \mu_B m_\ell B$

其中 $\mu_B = \gamma_e \hbar = -\dfrac{e\hbar}{2m_e}$ (Bohr magneton)



所以 p orbital 在沒有磁場作用下譜線不會split,但在磁場作用下卻split 成3條。

σ *line* 為 *circularly – polarized* , π *line* 為 *plane – polarized*

事實上 electron spin magnetic moment 亦會和外加磁場作用產生Zeeman splitting, 例如ESR（Electron Spin Resonance) 就是利用此原理 。

其中 $E = -\mu_z B = -g_e r_e m_s \hbar B = g_e \mu_B m_s B$

for electron $g_e = 2.0023$, called g factor

若是有多個電子，則以 $M_S = m_{S_1} + m_{S_2} + m_{S_3} + \ldots\ldots$ 代之

Nuclear spin magnetic moment亦會和外加磁場作用產生Zeeman splitting, 例如NMR（Nuclear Magnetic Resonance) 就是利用此原理 。 但其 $\boxed{\mu_B = \frac{+e\hbar}{2M_p}}$

因為是質子，重量很大，所以作用能很小，所需要外加磁場很大。