

Chapter 9.

Atomic structure and atomic spectra

-The structure and spectra of hydrogenic atom

-The structures of many e^- atom

-The spectra of complex atoms

The structure and spectra of hydrogenic atom

9.1 The structure of hydrogenic atoms

9.2 Atomic orbitals and their energies

9.3 Spectroscopic transitions and selection rules

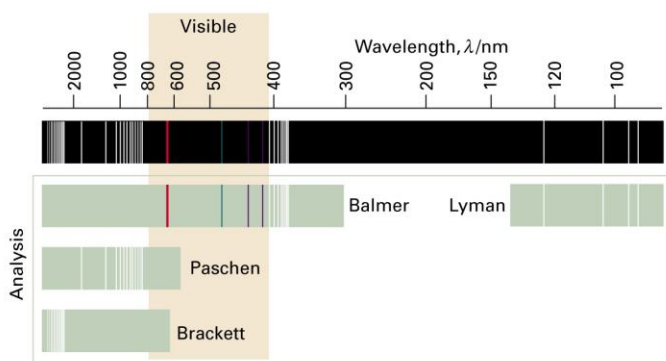
hydrogenic atoms:

H, He⁺, Li²⁺, U⁹¹⁺

many-electron atom:

The spectrum of atomic hydrogen

electric discharge — gaseous hydrogen —→ excited H atoms with light of discrete freq.

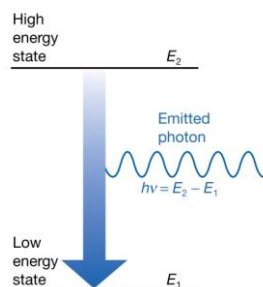


Note) Balmer series ~ the visible region

Balmer series: vis

$$\tilde{\nu} \propto \frac{1}{2^2} - \frac{1}{n^2} \quad n = 3, 4, \dots$$

Lyman: uv
Paschen: IR



Rydberg

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad R_H = 109\,677 \text{ cm}^{-1}$$

Each spectral line:

$$T_n = \frac{R_H}{n^2}$$

Ritz combination principle: wavenumber of any spectral line
is the difference between two terms

$$\tilde{\nu} = T_1 - T_2$$

Bohr freq condition (fig 13.2)

$$h\nu = E_2 - E_1$$

$$\Delta E = hcT_1 - hcT_2$$

$$\nu = cT_1 - cT_2$$

$$\tilde{\nu} = 1/\lambda = T_1 - T_2$$

9.1 The structure of hydrogenic atoms

Coulomb potential E of an electron in a hydrogenic atom
(with atomic number Z)

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The separation of internal motion,
For the e^- and a nucleus of mass m_N :

$$H = \hat{E}_{K,\text{electron}} + \hat{E}_{K,\text{nucleus}} + \hat{V} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

Reduced mass
For, electron and nucleus... $1/\mu \sim 1/m_e$

The total E of the two particles is

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V \quad \begin{array}{l} p_1 = m_1 \dot{x}_1 \\ p_2 = m_2 \dot{x}_2 \end{array}$$

The center of mass is

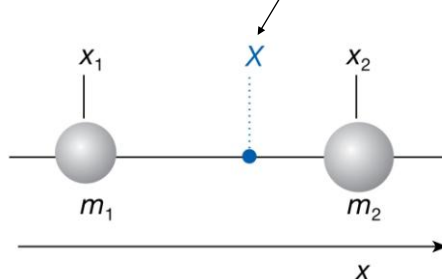
$$X = \frac{m_1}{m} x_1 + \frac{m_2}{m} x_2 \quad m = m_1 + m_2$$

The separation of two particles is

$$x = x_1 - x_2$$

relative motion

Translation of the center of mass



Internal relative coordinate...

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$

since potential E is centrosymmetric
(indep. of angle)

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

$$\Lambda^2 Y = -l(l+1)Y$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right) + V_{\text{eff}} R = ER$$

where

$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

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

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

multiply by r^2 / RY

$$-\frac{\hbar^2}{2\mu R} \left(r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} \right) + Vr^2 - \frac{\hbar^2}{2\mu Y} \Lambda^2 Y = ER^2$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right) + V_{\text{eff}} R = ER$$

radial wave eqn

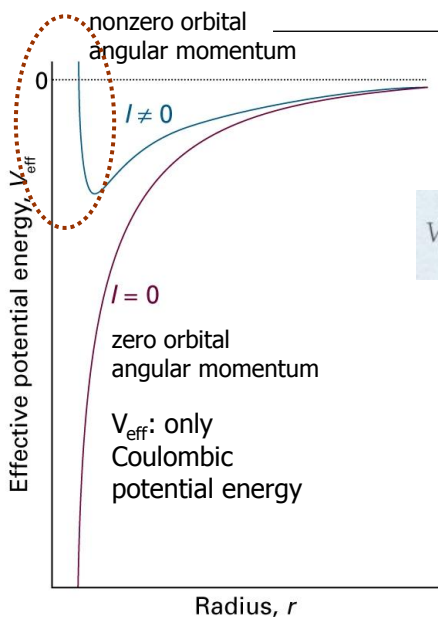
$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

constant

$$\frac{\hbar^2 l(l+1)}{2\mu}$$

$$\Lambda^2 Y = -l(l+1)Y$$

spherical harmonics



V_{eff} :
Coulombic potential energy +
non-zero centrifugal force

$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Coulombic
: attractive

centrifugal
: repulsive

$l=0, l\neq 0$ wavefunctions are very different near the nucleus.

- 9.2 The effective potential energy of an electron in the hydrogen atom.

by solving radial eqn (dep on l),

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

Radial wavefunction (dep on n, l not on m_l) is

$$R(r) = (\text{polynomial in } r) \times (\text{decaying exponential in } r)$$

These two ftns can be simply written with

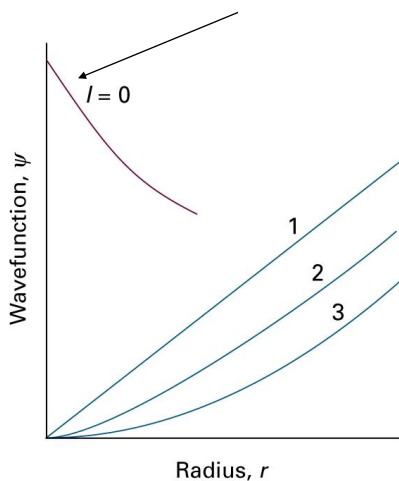
$$\rho = \frac{2Zr}{a_0} \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

Bohr radius: 52.9 pm
(from Bohr's early model of H atom)

$$R_{n,l}(r) = N_{n,l} \left(\frac{\rho}{n}\right)^l L_{n,l}(\rho) e^{-\rho/2n}$$

Laguerre polynomial

s orbitals has finite non-zero value at the nucleus



9.3

close to nucleus,
p orbitals are proportional to r ,
d orbitals are proportional to r^2 ,
f orbitals are proportional to r^3 ,

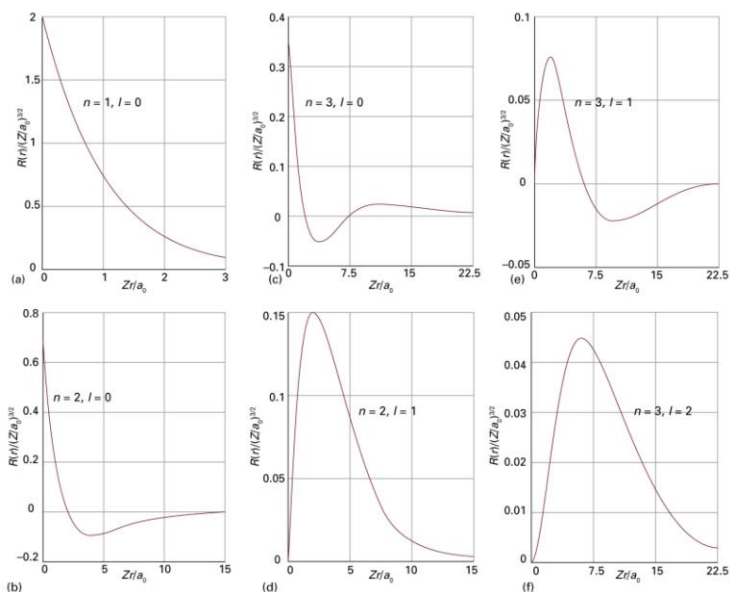
electrons are progressively excluded from
the nucleus

Table 9.1 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
1s	1	0	$2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2p	2	1	$\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$
3s	3	0	$\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)e^{-\rho/2}$
3p	3	1	$\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$
3d	3	2	$\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$ with $a = 4\pi\epsilon_0\hbar^2/\mu e^2$. For an infinitely heavy nucleus (or one that may be assumed to be so), $\mu = m_e$ and $a = a_0$, the Bohr radius. The full wavefunction is obtained by multiplying R by the appropriate Y given in Table 8.2.

Note) all R is 0 at the nucleus unless $l=0$ ($R \sim \rho^l$)



9.4 The radial wavefunctions of the few states of hydrogenic atoms of atomic number Z .

Note the s orbitals have a nonzero and finite value at the nucleus.

The horizontal scales are different in each: orbitals with high principal quantum numbers are relatively distant from the nucleus.

9.2 Atomic orbitals and their energies

Atomic orbitals

$$n, l, m_l \quad \psi_{n,l,m_l} \quad |n, l, m_l\rangle$$

$$\text{ex) } \psi_{1,0,0} \quad |1, 0, 0\rangle$$

n : principal quantum number
(from radial eqn)

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

l : angular momentum quantum number $\{l(l+1)\}^{1/2} \hbar$
(l : 0, 1, 2, 3, ..., $n-1$)

m_l : magnetic quantum number
z-component angular momentum
(m_l : $-l, \dots, 0, \dots, l$)

$$m_l \hbar$$

spin

S and m_s : for electron $-1/2, 1/2$

for electron in H, n, l, m_l, m_s

E-levels

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

$$hcR_H = \frac{\mu_H e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$$

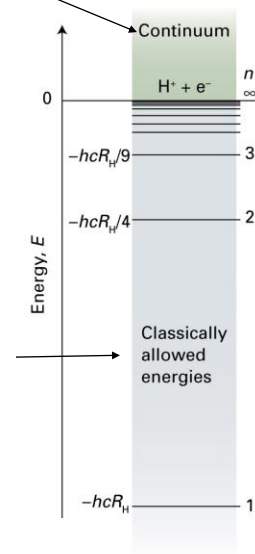
Rydberg constant

$$R_H = \frac{\mu_H R}{m_e} \quad R = \frac{m_e e^4}{8\epsilon_0^2 \hbar^3 c}$$

unbound state
:continuous

E separation is
proportional to Z^2
ex. H ($Z=1$)
He⁺ ($Z=2$)

bound state
:quantized



- 9.5 The energy levels of a hydrogen atom. The values are relative to an infinitely separated, stationary electron and a proton.

Ionization Energies

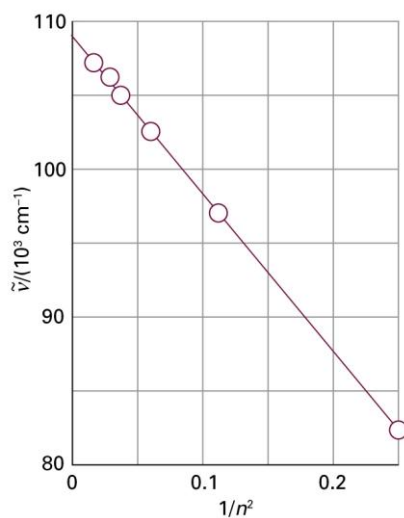
ionization E (I): the minimum E required
to remove an electron from the ground state

the ground state of H (n=1)

$$E_1 = -hcR_H$$

ionization E (n=∞)

$$I = hcR_H$$



- 9.6 The plot of the data in Examples 9.1 used to determine the ionization energy of an atom

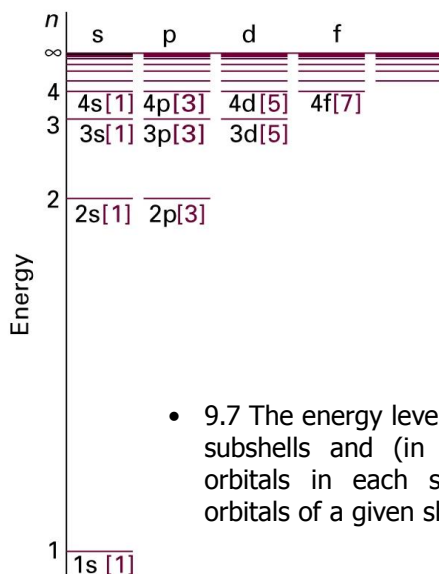
Shells and subshells

shell

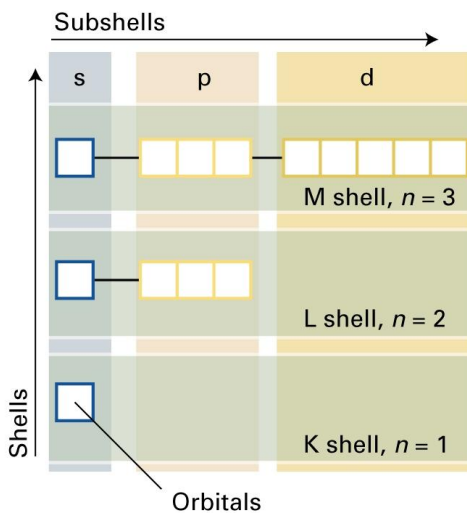
n= 1 2 3 4 ...
K L M N ...

subshell

l= 0 1 2 3 4 5 6...
s p d f g h i...



- 9.7 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy.



How many (in a shell)?

... n^2 degenerate states

9.8. The organization of orbitals (white squares) into subshells (characterized by l) and shells (characterized by n)

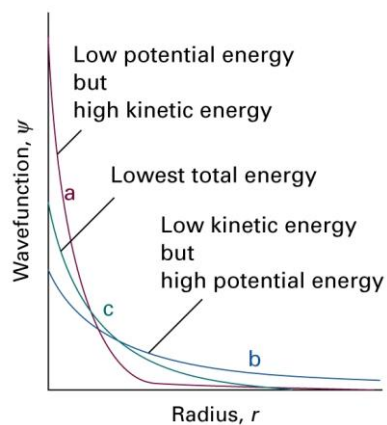
Atomic orbitals (1)

s orbitals: $n=0, l=0, m_l=0$

For $Z=1,$

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

All s-orbitals are spherically symmetric, but differ in the number of nodes.



Atomic orbitals (2)

All s-orbitals are spherically symmetric, but differ in the number of nodes.

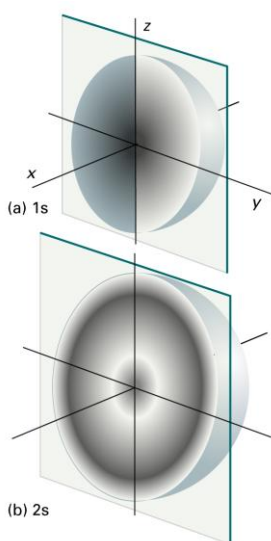
Ex) s has node at ...

$$\text{For } 2s, \quad 2 - \frac{\rho}{2} = 0 \text{ at } \rho = 4, \text{ which means } r = \frac{2a_0}{Z}$$

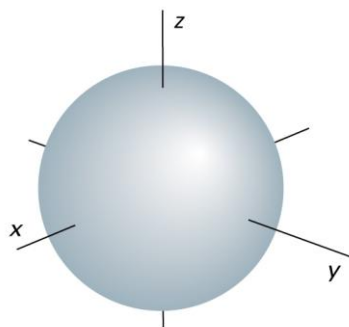
$$\text{For } 3s, \quad 6 - 2\rho + \left(\frac{1}{3}\rho\right)^2 = 0$$

The E of s-orbital increases because the avg distance of e- increases with n

According to virial theorem, $\langle E_k \rangle = -\frac{1}{2}\langle V \rangle$
 so, total E_k increases although avg. E decreases with n



9.10 Representations of the (a) 1s and (b) 2s hydrogenic atomic orbitals in term of their electron densities (as represented by the density of shading).



9.11 The boundary surface of an s orbital, within which there is a 90 per cent probability of finding the electron.

Radial distribution functions

$$|\psi|^2 \propto e^{-2Zr/a_0}$$

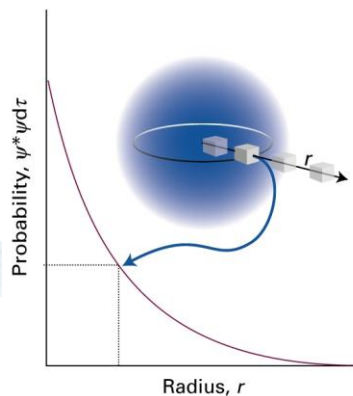
$$P(r) = 4\pi r^2 \psi^2$$

For orbitals that are not spherically symmetrical,

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

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

➔ most probable radius occurs at Bohr radius

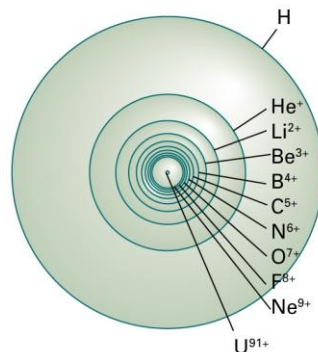
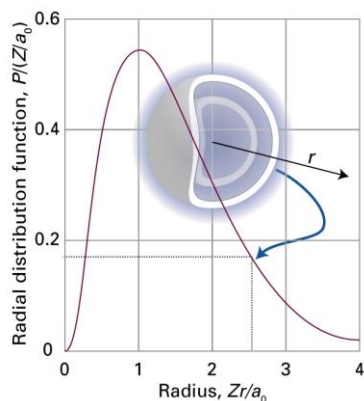


For orbitals that are not spherically symmetrical,

$$\psi = RY \text{ is } |RY|^2 d\tau \text{ with } d\tau = r^2 dr \sin\theta d\theta d\phi$$

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

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



- 9.13. The radial distribution function p gives the probability that the electron will be found anywhere in a shell of radius r . for a $1s$ electron in hydrogen, P is a maximum when r is equal to the Bohr radius a . The value of P is equivalent to the reading that a detector shaped like a spherical shell would give as its radius varied.

p orbitals

- non-zero angular momentum
- zero amplitude at $r=0$
- difference from s -orbitals (d, f, \dots)

CM view:

centrifugal effect (making e^- away from the nucleus)

$V_{\text{eff}}(r \rightarrow 0) \rightarrow \text{infinity}$

p orbitals: $l=1, m_l=-1, 0, 1$

same momentum, and different z-axis momentum

p_z orbitals: $m_l=0$

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

$$\psi_{p_z} = zf(r)$$

$m_l = \pm 1$, non-zero z-axis angular momentum

wavefns with ϕ dep.

$e^{i\phi}$ CW rotation
viewed
from below

$$\psi_{p_{\pm 1}} = R_{2,1}(r)Y_{1,\pm 1}(\theta, \phi) = \mp \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \sin \theta e^{\pm i\phi} = \mp \frac{1}{2^{1/2}} r \sin \theta e^{\pm i\phi} f(r)$$

$P_{x,y}$ orbitals:

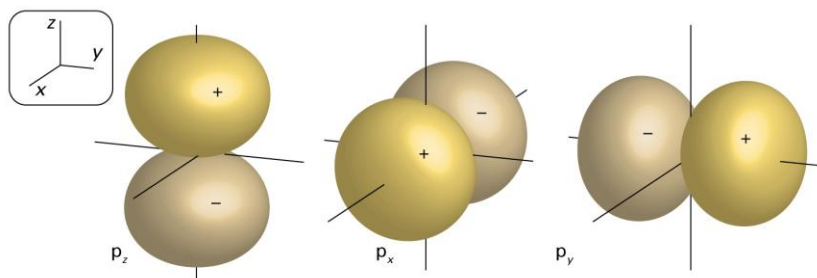
$$\psi_{p_x} = \frac{1}{2^{1/2}} (p_{+1} - p_{-1}) = r \sin \theta \cos \phi f(r) = xf(r)$$

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

• $m_l=0$

the same around ϕ

• no net orbital angular momentum
around z-axis

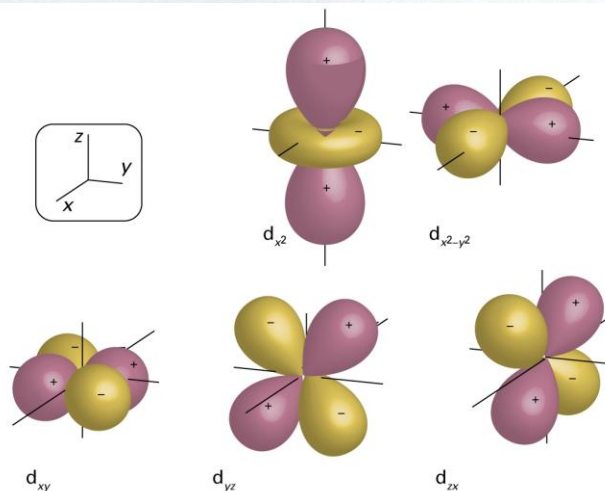


9.15 The boundary surfaces of p orbitals. A nodal plane passed through the nucleus and separates the two lobes of each orbital.

d orbitals

d-orbitals: $n=3, l=0,1,2, m_l=-2,-1,0,1,2$

$$\begin{aligned} d_{xy} &= xyf(r) & d_{yz} &= yzf(r) & d_{zx} &= zxf(r) \\ d_{x^2-y^2} &= \frac{1}{2}(x^2 - y^2)f(r) & d_{z^2} &= (1/2\sqrt{3})(3z^2 - r^2)f(r) \end{aligned}$$



9.3 Spectroscopic transitions and selection rules

Transition

Is the transition "allowed" to any state?

ex) from $|n_1, l_1, m_{l1}\rangle$ to $|n_2, l_2, m_{l2}\rangle$

NO!!!

because the change in angular momentum of the electron must compensate for the angular momentum of a photon (a photon has intrinsic $s=1$)

ex) from d ($l=2$) to s ($l=0$) is not available.

➡ Selection rule for H: $\Delta l = \pm 1, \Delta m_l = 0, \pm 1$

n can change by any amount since it is not related to "angular momentum"

the transition rate \sim [transition dipole moment]²

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

$$\mu_{fi}$$

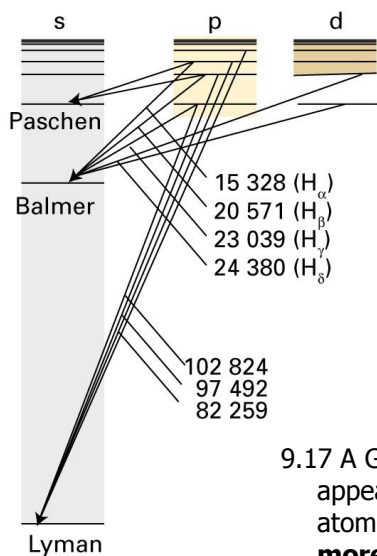
$$\mu_x = -ex, \mu_y = -ey, \text{ and } \mu_z = -ez.$$

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

$$z = (4\pi/3)^{1/2} r Y_{1,0}$$

$$\int \psi_f^* z \psi_i d\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty R_{n_f, l_f} r R_{n_i, l_i} r^2 dr \int_0^\pi Y_{l_f, m_{l_f}}^* Y_{1,0} Y_{l_i, m_{l_i}} \sin\theta d\theta d\phi$$

this will be zero
unless $l_f = l_i \pm 1, m_{l_f} = m_{l_i} \pm m$



9.17 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. **The thicker the line, the more intense the transition.**

The structure of many electron atoms
-Schrodinger eqn is not analytical

9.4 The orbital approximation

9.5 Self-consistent field orbitals

9.4 The orbital approximation

ex) He

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \dots$$

$$H = H_1 + H_2$$

$$E = E_1 + E_2$$

$$\begin{aligned} H\Psi(\mathbf{r}_1, \mathbf{r}_2) &= (H_1 + H_2)\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) = H_1\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) + \psi(\mathbf{r}_1)H_2\psi(\mathbf{r}_2) \\ &= E_1\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) + \psi(\mathbf{r}_1)E_2\psi(\mathbf{r}_2) = (E_1 + E_2)\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \\ &= E\Psi(\mathbf{r}_1, \mathbf{r}_2) \end{aligned}$$

The He atom

- Configuration

H: $1s^1$

He: $1s^2$

• Pauli exclusion principle :

No more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spins must be paired

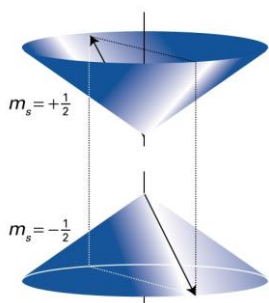


Fig. 9. 18
Electrons with paired spins
have zero resultant spin
angular momentum.

- The Pauli exclusion principle applies to any pair of identical fermions but not to bosons...

- The Pauli exclusion principle is a part of Pauli principle

• 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 remains same.

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

We need to consider total wave function (include spins...), not overall wave function

$$\sigma_+(1, 2) = (1/\sqrt{2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$

$$\sigma_-(1, 2) = (1/\sqrt{2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

$$\times \psi(1)\psi(2)\alpha(1)\alpha(2)$$

$$\times \psi(1)\psi(2)\beta(1)\beta(2)$$

$$\times \psi(1)\psi(2)\sigma_+(1, 2)$$

$$\rightarrow \psi(1)\psi(2)\sigma_-(1, 2)$$

$$\sigma_+(1, 2) = (1/\sqrt{2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} = \sigma_+(2, 1)$$

$$\sigma_-(2, 1) = (1/\sqrt{2})\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\}$$

$$= -(1/\sqrt{2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_-(1, 2)$$

Only one survives!!!

Penetration and shielding

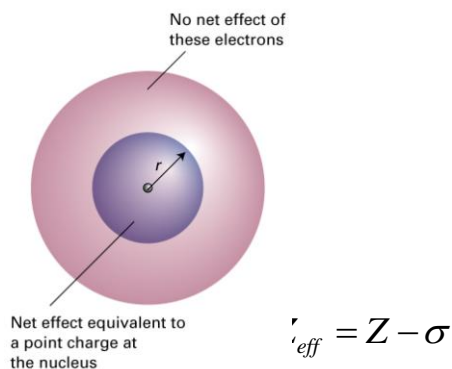


Table 9.2* Effective nuclear charge, $Z_{\text{eff}} = Z - \sigma$

Element	Z	Orbital	Z_{eff}
He	2	1s	1.6875
C	6	1s	5.6727
		2s	3.2166
		2p	3.1358

* More values are given in the Data section.

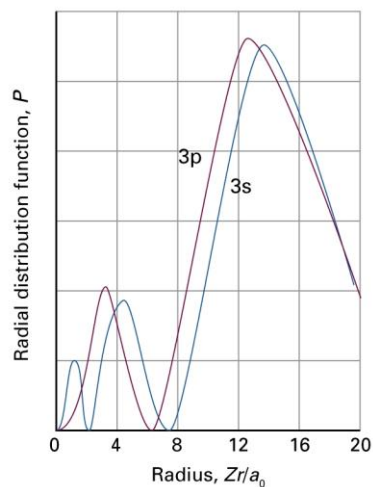
9.19 An electron at a distance r from the nucleus experiences a Coulombic repulsion from all the electrons within a sphere of radius r and which is equivalent to a point negative charge located on the nucleus. The negative charge reduces the effective nuclear charge of the nucleus from Z to Z_{eff}

9.20

- s orbital (here a 3s orbital) is closer to the nucleus than p orbital.
- s electron experiences less shielding and is more tightly bound than a p electron.

The E of subshell in a many e atom
: s<p<d<f

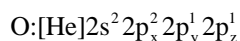
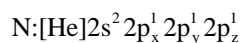
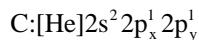
Valence electron: largely responsible
for chemical bonds



The building-up principle

- 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s
- Building-up principles

Electrons occupy different orbitals of a given subshell before doubly occupying any one of them



- Hund's maximum multiplicity rule

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

spin correlation

e- with parallel spins behave

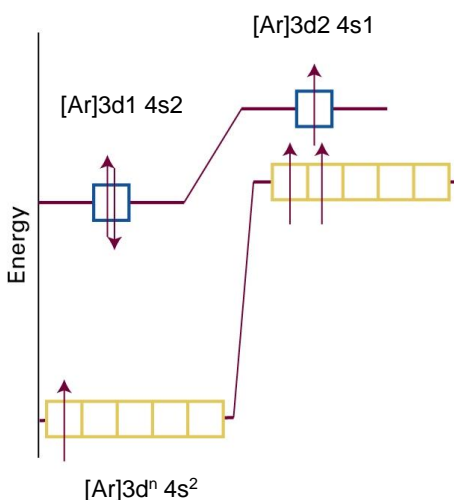
as if they have a tendency to stay well apart and repel each other less

$$\Psi = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

$$\Psi_+ = (1/2^{1/2})\{\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\}$$

$$\mathbf{r}_1 = \mathbf{r}_2$$

Sc (Scandium)



- two 3d e- repel each other strongly than two 4s

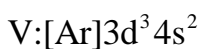
9.21 **Strong electron-electron repulsions in the 3d orbitals are minimized** in the ground state of Sc (Scandium) if the atom has the configuration [Ar]3d¹ 4s² (shown on the left) instead of [Ar]3d² 4s¹ (shown on the right). The total energy of the atom is lower when it has the [Ar]3d¹ 4s² configuration despite the cost of populating the high-energy 4s orbital.

How about Ga?

-rich inorganic d-metal chemistry

The configurations of ions

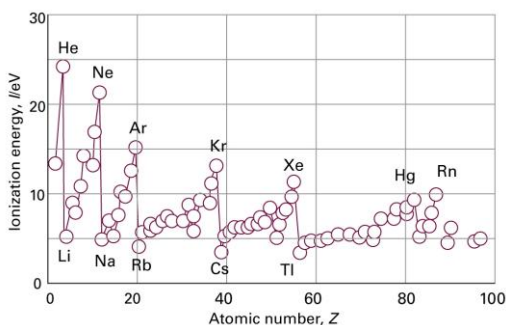
-how e⁻ is removed



- why not $\text{V}^{2+}: [\text{Ar}]3d^1 4s^2$?
Not clearly understood
- calculation shows that for a sufficiently large Z_{eff} e-e repulsions are compensated by attractive interaction betw N and e

E of [Ar]3d³ is lower than that of [Ar]3d¹4s²

Ionization energy and electron affinities



9.22 The first ionization energies of the elements plotted against atomic number.

Table 9.3* First and second ionization energies

Element	$I_1/(\text{kJ mol}^{-1})$	$I_2/(\text{kJ mol}^{-1})$
H	1312	
He	2372	5251
Mg	738	1451
Na	496	4562

* More values are given in the Data section.

I_1 : 1st ionization E
 I_2 : 2nd ionization E
 (remove 2nd e⁻ from the singly charged cation)

•Standard enthalpy of ionization

$$\Delta_{\text{ion}} H^\ominus(T) = I + \frac{5}{2}RT$$



$$\Delta_r H^\ominus(T) = \Delta_r H^\ominus(0) + \int_0^T \Delta_r C_p^\ominus dT$$

$$\Delta_r C_p^\ominus = +\frac{5}{2}R.$$

$$\Delta_{\text{ion}} H^\ominus(T) = I + \frac{5}{2}RT$$

$$\Delta_r H^\ominus(T) = I_1 + I_2 + 5RT$$

•Electron affinity:

E released when an e⁻ attaches to a gas phase atom

standard enthalpy of e⁻ gain

$$\Delta_{\text{e}^-\text{g}} H^\ominus(T) = -E_{\text{ea}} - \frac{5}{2}RT$$

$$\Delta_{\text{r}g} H^\ominus(X) = -\Delta_{\text{ion}} H^\ominus(X^-)$$

Table 9.4* Electron affinities, $E_a/(\text{kJ mol}^{-1})$

Cl	349		
F	322		
H	73		
O	141	O ⁻	-844

* More values are given in the Data section.

Li: a low 1st ionization E due to the shielding of outermost e from nucleus ($Z_{\text{eff}} \sim 1.3$, $Z=3$)

decrease of ionization E from Be to B:
~outermost e of B is 2p (less tight than 2s)

increase of ionization E from B to C:
~outermost e of C is also 2p

decrease of ionization E from C to N:
~further increase in nuclear charge

decrease of ionization E from N to O:
a 2p in O must be doubly occupied and e-e repulsions are increased. In addition, the loss of 2p is quite stable (like N)

decrease of ionization E from Ne to Na:
3s is too far from nucleus. (well shielded by Ne-like core)

E_{ea} of anion is negative (endothermic)
-greatest close to chlorine (complete the valence shell and strongly interact w/ nucleus)

E_{ea} of cation is small and may be negative

9.5. Self-consistent field orbitals

- For many electron system,

$$V = -\sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{1}{2} \sum_{i,j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad i \neq j$$

- hopeless to solve analytically

Hartree-Fock SCF (1)

for 2p orbital

let's assume that we are interested in 2p

Potential (e-N)

$$-\frac{\hbar^2}{2m_e} \nabla_1^2 \psi_{2p}(r_1) - \frac{Ze^2}{4\pi\epsilon_0 r_1} \psi_{2p}(r_1)$$

Coulomb operator:
 E_p of e- of interest due to the charge density of the e- in the other occupied orbitals $-e|\psi_i(r_2)|^2$

$$+ \frac{e^2}{2\pi\epsilon_0} \left\{ \sum_i \int \frac{\psi_i(r_2)^* \psi_i(r_2)}{r_{12}} d\tau_2 \right\} \psi_{2p}(r_1$$

Hartree-Fock orbitals

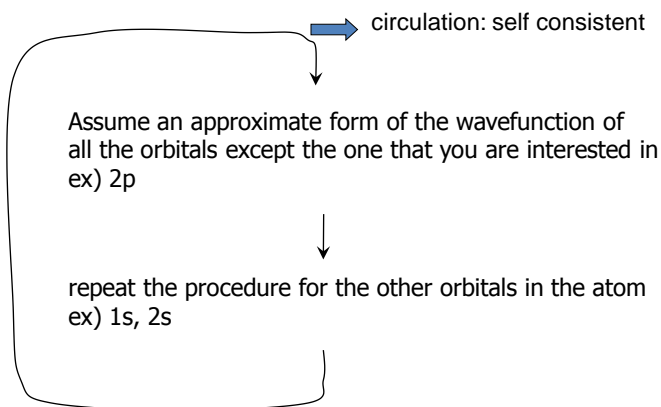
orbitals

$$- \frac{e^2}{4\pi\epsilon_0} \left\{ \sum_i \int \frac{\psi_i(r_2)^* \psi_{2p}(r_2)}{r_{12}} d\tau_2 \right\} \psi_i(r_1)$$

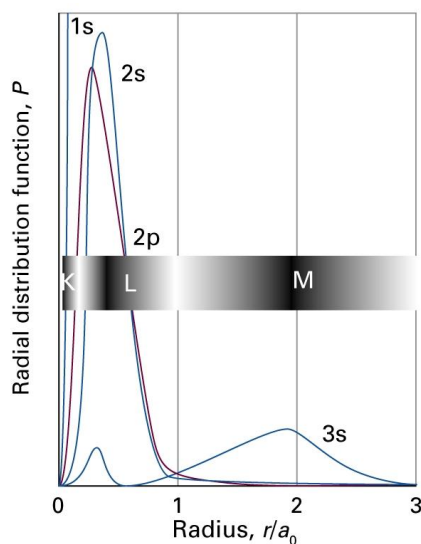
Exchange operator:
spin correlation effects

$$= E_{2p} \psi_{2p}(r_1)$$

Hartree-Fock SCF (2)



circulation until the difference
betw. the previous and the present calculation is insignificant



9.23 The radial distribution functions for the orbitals of Na based on SCF calculations. Note the shell-like structure, with the 3s orbital outside inner K and L shells.

The spectra of complex atoms

9.6 Linewidths

9.7 Quantum defects and ionization limits

9.8 Singlet and triplet states

9.9 Spin-orbit coupling

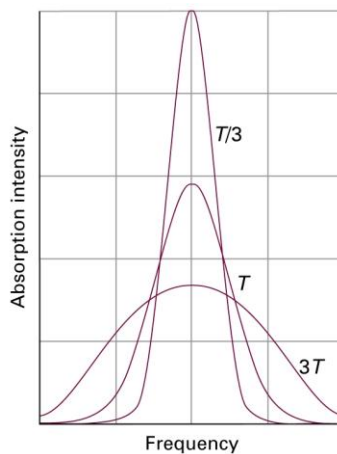
9.10 Term symbols and selection rules

9.6 Linewidths

-Doppler broadening

-Lifetime broadening

9.24 Gaussian shape of Doppler-broadened spectral line~Maxwell distribution of speeds in the sample



9.7 Quantum defects and ionization limits

- Total E of many e- atoms do not in general vary as $1/n^2$
- the outermost e-: $Z_{\text{eff}} \sim$ slightly larger than 1
- Quantum defect δ : $-hcR/(n-\delta)^2$
- Rydberg state: some excited state that $1/n^2$ relationship is valid

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

9.8 Singlet and triplet states

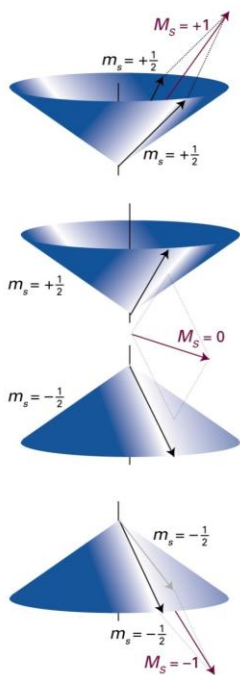
for He: $1s^2 \longrightarrow 1s^1 2s^1$ parallel
or antiparallel
↑
gnd state

- antiparallel (paired), zero net spin, singlet
(higher E: Hund's maximum multiplicity rule)

$$\sigma_-(1, 2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

- parallel (paired), triplet
(lower E: Hund's maximum multiplicity rule)

$$\begin{array}{ccc} \alpha(1)\alpha(2) & \sigma_+(1, 2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} & \beta(1)\beta(2) \\ \uparrow & \uparrow & \uparrow \\ \text{nonzero} & \text{zero net spin} & \text{nonzero} \end{array}$$



9.25

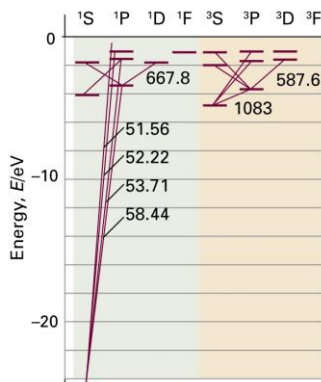
for He: 2 electrons parallel spins

the angle between the vector is the same in all three cases

for all three arrangements:
the same total spin angular momentum
(the two vectors has the same length, but
points in different directions).

- two 'parallel' spins are not strictly parallel.

- Coulombic interxn between e-s in an atom is strong, E difference between singlet and triplet can be large
- for states arising from the same configuration, the triplet state generally lies lower than the singlet states



"simple" helium atom.

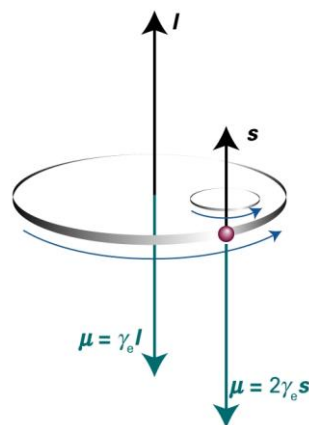
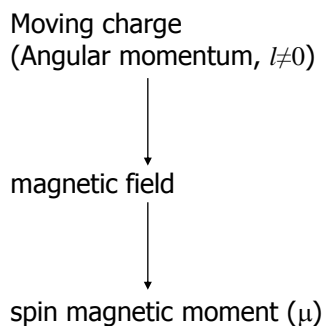
1. only 1 e- is excited
(Excitation of 2e- requires E greater than IE)
2. no radiative transition between singlet and triplet states

9.26 Part of the Grotrian diagram for a helium atom. Note that there are

no transitions between the **singlet** and **triplet** levels.

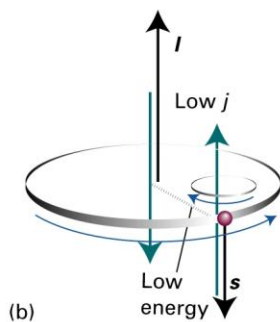
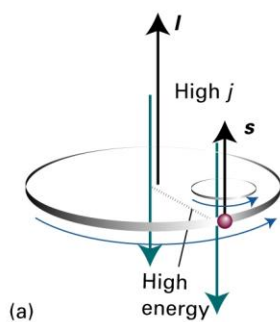
(no change in the relative orientation of the two electron spins)

9.9. Spin-orbit coupling



9.27

For an electron, the magnetic moment is antiparallel to the orbital angular momentum, but proportional to it. For spin angular momentum, there is a factor 2, which increases the magnetic moment to twice its expected value



9.28

- Spin-orbit coupling: magnetic interaction between spin and orbital magnetic moments.

(a) parallel angular momenta: the magnetic moments are aligned unfavourably

(b) opposed angular momenta: favourable.

This magnetic coupling is the cause of the splitting of a configuration into levels.

Total angular momentum

- the **dependence** of the **spin-orbit interaction** on the **relative orientations of the spin and orbital angular momenta**
- \sim the vector sum of its spin and orbital momenta

- when spin and angular momenta are nearly parallel, total angular momenta is high
- j and m_j
- $j=l+1/2$: same direction
- $j=l-1/2$: opposite direction
- for $l=1$
- $j=3/2$: same direction
- $j=1/2$: opposite direction

note) when $l=0$,

- the only permitted j is $1/2$
- (total angular momenta = spin angular momenta, no orbital angular momenta)

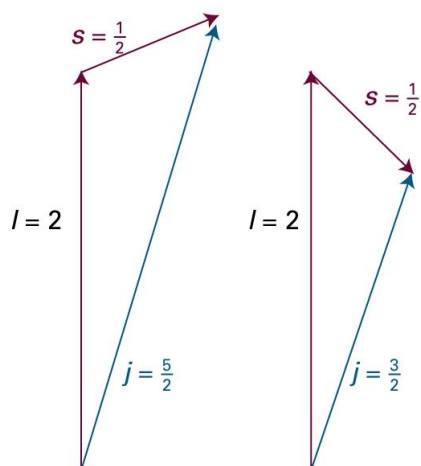


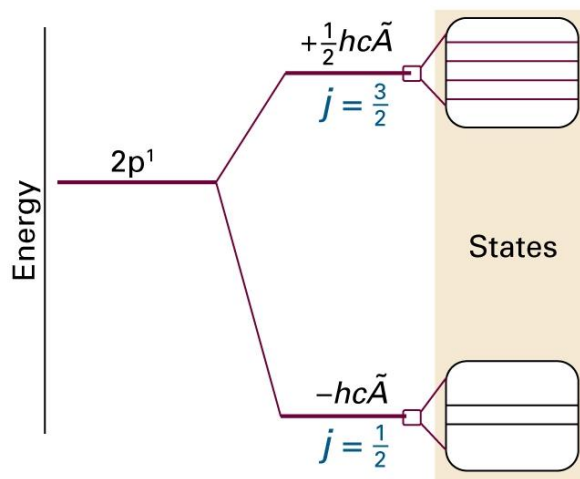
Fig. 9.29.

The coupling of the spin and orbital angular momenta of d electron ($l=2$):

two possible values of j (depending on the **relative orientations** of the **spin** and **orbital angular momenta** of the electron).

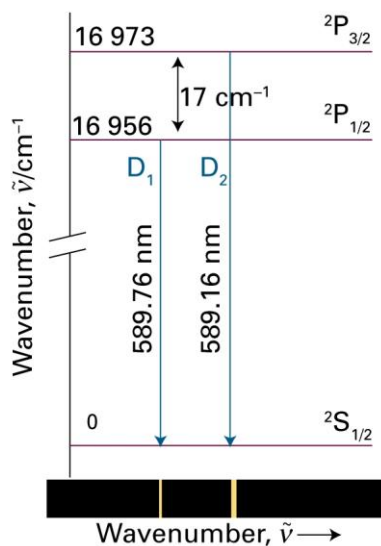
- Spin-orbit coupling constant

$$E_{l,s,j} = \frac{1}{2}hc\tilde{A}\{j(j+1) - l(l+1) - s(s+1)\}$$



9.30 The levels of a P term arising from spin-orbit coupling. Note that the low- j level lies below the high- j level energy.

Fine structure



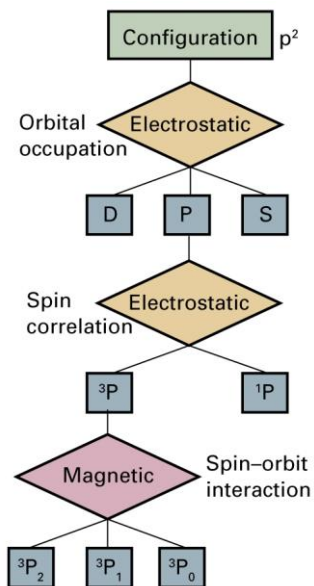
9.31 The energy-level diagram for the formation of the **sodium D lines**. The splitting of the spectral lines (by 17 /cm) reflects the splitting of the levels of the P term.

9.10. Term symbols and selection rules

Term symbols

multiplicity $(2S+1)$ $\{L\}$ total angular momentum QN (J)

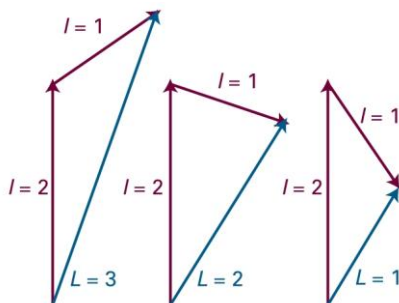
total orbital momentum quantum number



9.32 A summary of the types of interaction that are responsible for the various kinds of splitting of energy levels in atoms. For light atoms, magnetic interaction are small, but in heavy atoms they may dominate the electrostatic (charge-charge) interactions.

total orbital angular momentum

- total orbital momentum quantum number, L
 $[L(L+1)]^{1/2} \hbar$
 $2L+1$ orientations, each orientation M_l
- total spin momentum quantum number, S , M_s
- total angular momentum quantum number, J , M_j



9.33 The total angular orbital momenta of a p electron and a d electron correspond to $L=3, 2$, and 1 reflect the different relative orientations of the two momenta.

Clebsch-Gordon series

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

Max: two orbital angular momenta are in the same direction

Min: two orbital angular momenta are in the opposite direction

intermediate: relative orientations

ex. for 2 p e- ($l_1=l_2=1$), $L=2,1,0$

L:	0	1	2	3	4	5	6...
	S	P	D	F	G	H	I...

closed shell: zero orbital angular momentum

-> we need to consider **only the e- of unfilled shell**

ex. $[\text{Ne}]3s^1$... only S

Multiplicity

multiplicity $(2S+1)$ $\{L\}$ total angular momentum QN (J)

S (total spin angular momentum QN):

- non-negative or half-integer
- $S=s_1+s_2, s_1+s_2-1, \dots, |s_1-s_2|$
- each e-: $s=1/2$

ex)

for 2 e-, $S=0, 1$

for 3 e-, $S=3/2, 1/2$

$S=0$ (ex. $1s^2$), 1S (singlet)

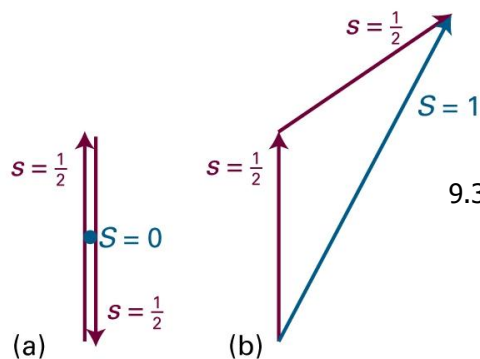
for single e-, (doublet)

$S=s=1/2$, $[\text{Ne}]3s^1 \dots ^2S$

$[\text{Ne}]3p^1 \dots ^2P$

for 2 unpaired e-,

$S=1$, $2S+1=3 \dots$ triplet 3D



9.34 For 2 electron (each of which has $s=1/2$), only two total spin states ($S=0,1$).

$S=0$ ($2S+1=1$):
only one M_s ($M_s=0$)
singlet (Fig 13.20)

$S=1$ ($2S+1=3$):
three M_s ($+1,0,-1$)
triplet (Fig 13.26)

Total angular momentum

multiplicity ($2S+1$) $\{L\}$ total angular momentum QN (J)

$J=j$, with $l+1/2$ or $|l-1/2|$

ex.

$[\text{Ne}]3s^1$: $j=1/2$ ($l=0, s=1/2$) ... $^2S_{1/2}$

$[\text{Ne}]3p^1$: $j=3/2$ or $1/2$ ($l=1, s=1/2$) ... $^2P_{3/2}$ or $^2P_{1/2}$

- Russell-Saunders coupling

when the spin-orbit coupling is weak
(low atomic number)

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

3D ($L=2, S=1$) ... [Ne]2p¹3p¹ ... permitted J are
3,2,1

-when $L > S$, multiplicity $(2S+1)$ = the number of level

ex. $^2P_{3/2}, ^2P_{1/2}, \dots, ^3D_3, ^3D_2, ^3D_1$

-when $L < S$, not applicable

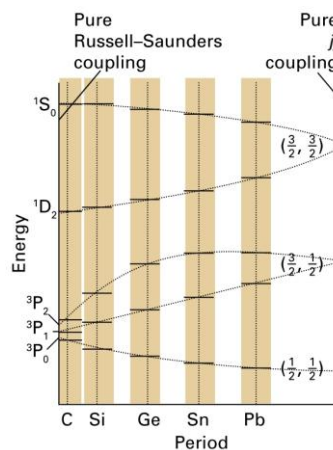
ex. $^2S_{1/2}$

- jj -coupling

- when the spin-orbit coupling is weak (for heavy atom)
- jj -coupling $\rightarrow J$
- each e⁻ as a particle with $j=3/2$ or $1/2$

ex. p^2

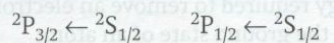
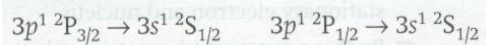
$j_1 = \frac{3}{2}$	and	$j_2 = \frac{3}{2}$	$J = 3, 2, 1, 0$
$j_1 = \frac{3}{2}$	and	$j_2 = \frac{1}{2}$	$J = 2, 1$
$j_1 = \frac{1}{2}$	and	$j_2 = \frac{3}{2}$	$J = 2, 1$
$j_1 = \frac{1}{2}$	and	$j_2 = \frac{1}{2}$	$J = 1, 0$



9.35 The correlation diagram for some of the states of a two-electron system. All atoms lie between the two extremes but, the heavier the atom, the closer it lies to the pure jj -coupling case.

Selection rules

-any spectral transition
ex. (Fig 9.31) yellow sodium doublet



Selection rule \sim conservation of **angular momentum**

for light atom,

light doesn't affect spin directly

overall orbital momentum change

$$\Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta l = \pm 1 \quad \Delta J = 0, \pm 1, \quad \text{but } J = 0 \leftrightarrow J = 0$$

orbital angular momentum must change