Atomic Structure and Atomic Spectra

Atomic Structure: Hydrogenic Atom

Reading: Atkins, Ch. 10 (7판 Ch. 13)

The principles of quantum mechanics → <u>internal structure of atoms</u>

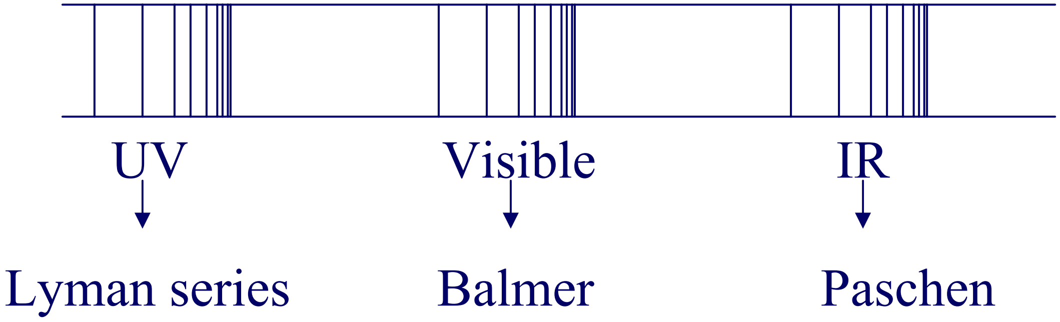
1. **Hydrogenic atom**: one electron atom or ion (e.g., H, He^+, Li^{2+}, U^{91+}) → Schrödinger equations can be solved exactly

2. Many electron atom: complicated but same principle

3. Atomic spectroscopy: experimental technique to determine the electronic structure of atoms

1. Hydrogenic atom: one electron atom or ion

(1) Spectrum of atomic hydrogen



UV → Lyman series

Visible → Balmer

IR → Paschen

Wavenumber $\nu = R_H(1/n_1^2 - 1/n_2^2)$, $R_H = 109677\ \text{cm}^{-1}$ (Rydberg constant)

$n_1 = 1$ (Lyman),
$n_1 = 2$ (Balmer),
$n_1 = 3$ (Paschen)

$n_2 = n_1 + 1, n_1 + 2$ ……

$h\nu = E_2 – E_1$ "energy quantization"

$h\nu = hc/\lambda =$ ν : frequency, λ : wavelength

- electromagnetic radiation is absorbed and emitted by atoms only at certain wavenumbers → certain energy states of atoms are permitted: “energy quantization”

(2) Wavefunction

- The Coulomb potential energy of an electron in atomic number Z hydrogenic atom (1-electron): nuclear charge Ze

$$V = -Ze^2/(4\pi \varepsilon_0 r)$$

r: distance electron from nucleus

ε_0: vacuum permittivity

- Hamiltonian for electron and nucleus, electron mass m_e, nucleus mass m_N

$$H = \hat{E}_{K,e^-} + \hat{E}_{k,n} + \hat{V}$$

$$= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_n}\nabla_n^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- internal motion of electron relative to the nucleus :

relative motion of electron and nucleus

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}, \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}, \quad \mu\text{: reduced mass}$$

$$m_n \gg m_e, \quad \frac{1}{\mu} \approx \frac{1}{m_e}, \quad \mu \cong m_e$$

Schrödinger equation, $H\Psi = E\Psi$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

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

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

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

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

Y: angular variables ⟶ constant

$\Lambda^2 Y = -l(l+1)Y$: Spherical harmonics (Table 9.3, (7판 12-3))

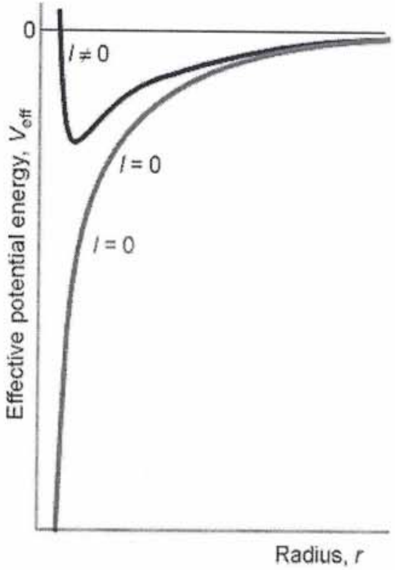
$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)+\left(\underbrace{-\frac{Ze^2}{4\pi\varepsilon_0 r}+\frac{l(l+1)\hbar^2}{2\mu r^2}}_{\equiv V_{eff}}\right)R=ER$$

→ radial wavefunction ; mass μ, potential energy V_{eff}, 1-D

$$V_{eff} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

↓ Coulomb potential energy of electron

↓ centrifugal force from angular momentum of electron around the nucleus



i) $l = 0$ → no angular momentum
→ V_{eff}: pure Coulombic & attractive

ii) $l = 0$ $r = 0$: repulsive term, $1/r^2$ dominates $\Rightarrow$
repulsion
$r = \infty$: similar to $l = 0$

Radial equation

$$R'' + \frac{2}{r}R' + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}\right) - \frac{l(l+1)}{r^2}\right] = 0$$

$$R_{n,l}(r) = \left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2} \cdot \left(\frac{2Z}{na_0}\right)^{l+\frac{3}{2}} \cdot r^l \cdot e^{-\frac{Zr}{na_0}} \cdot L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$: associated Laguerre functions

$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$: Bohr radius (52.9177 pm)

Table 10.1 (7판 13.1) Hydrogenic radial wavefunctions

Full wavefunction:

Ψ = RY (**Y: Table 9.3, R: Table 10.1**)

$n = 1, 2, 3\ldots\ldots, \quad n \geq l + 1$

$\rightarrow \quad l = 0, 1, 2, \ldots\ldots n-1$

Radial wavefunction

- Energy

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \cdot \frac{1}{n^2}$$

$l \neq 0 \rightarrow R_{n,l} = 0$ at the nucleus $(\because R \propto \rho^l)$

$\Psi = RY$

$n = 1, l = 0, m_l = 0,$ $\Psi_{100}(r, \theta, \phi) = R_{10}(r)Y0_0(\theta, \phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$

3 quantum numbers
$n = 1, 2, 3 \ldots\ldots\ldots$
$l = 0, 1, 2, 3 \ldots\ldots n-1$
$m_l = -l, -l+1, \ldots 0, \ldots\ldots l-1, l$

(3) Atomic orbital: a one-electron wavefunction for an electron in an atom

- define orbital as the state $|n, l, m_l>$

$$\Psi_{1,0,0} \Rightarrow |1, 0, 0> \Rightarrow n = 1, l = 0, m_l = 0$$

- Quantum numbers (n, l, m_l, m_s)

i) Principle quantum number (n), $n = 1,2,3\ldots..$

$\Rightarrow$ Determine the energy of the electron

ii) Angular momentum quantum number (l), $l = 0,1,2,3\ldots(n-1)$

$\Rightarrow$ Electron with l has an angular momentum of magnitude $[l(l + 1)]^{1/2}\,\hbar$

iii) Magnetic quantum number (m_l), $m_l = 0, \pm1, \pm2, \pm3,\ldots.$

$\Rightarrow$ Electron quantum number m_l has a z-component of angular momentum $m_l\hbar$

iv) Spin magnetic quantum number (m_s)

$\Rightarrow$ Intrinsic angular momentum by two quantum numbers s,

$$s = ½, m_s = \pm ½$$

$E_n = -hcR/n^2$, $hcR =$

$E \propto Z^2$,

He^+ $(Z = 2)$: 4 x H $(Z = 1)$

Ionization energy : excited to $n = \infty$

$I = hcR_H = 13.60$ eV for H

Shell, $n = 1, \quad 2, \quad 3, \quad 4, \ldots..$
K L M N

Subshell $l = 0, \quad 1, \quad 2, \quad 3, \quad 4, \quad \ldots.$
s p d f g h i

(i) s orbitals

- n =1, $l = 0$, $m_l = 0$ (1s)

$$\Psi_{1,0,0} = R_{1,0}\, Y_{0,0} =$$

$\Rightarrow$ Independent of angle, same value
at all points of constant radius

Probability at r = 0 $\Rightarrow$ $1/\pi a_0^3$

All s orbitals $\Rightarrow$ spherically symmetric,
but differ in number of radial nodes

- 2s: n = 2, $l = 0$, $m_l = 0$

$$\Psi_{2s} =$$

node at $2 - r/a_0 = 0 \rightarrow r = 2a_0/Z$

- 3s: $n = 3, l = 0, m_l = 0$

Node: $1.9a_0/Z$ and $7.1a_0/Z$

- probability on a spherical shell of thickness dr at radius r

radial distribution function

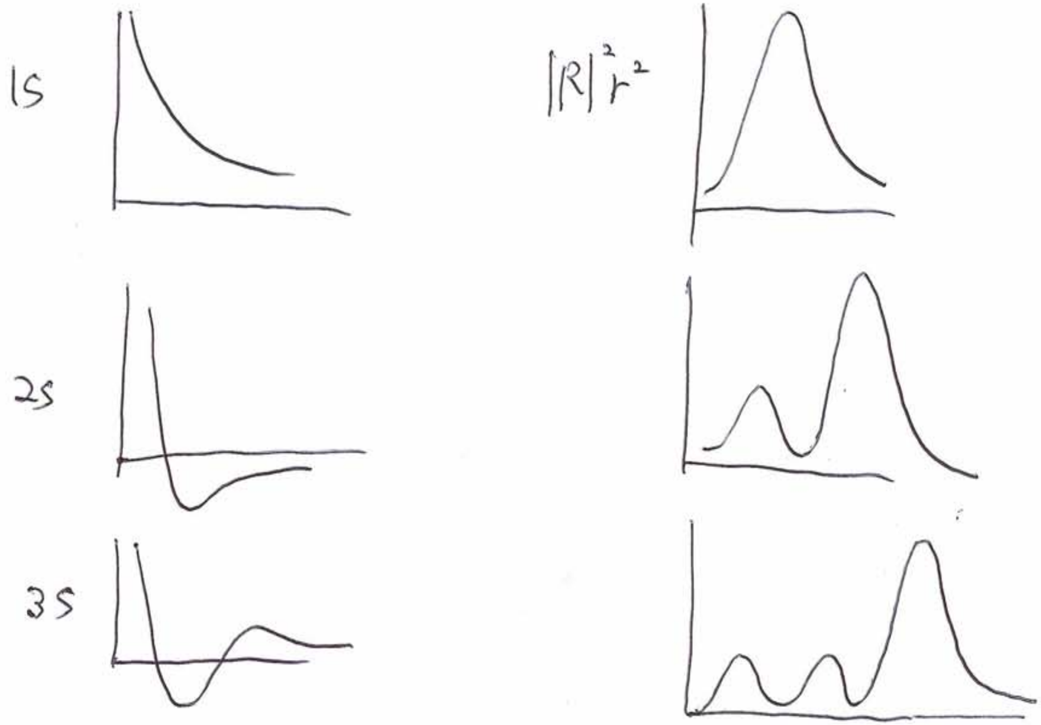
$$P(r) = 4\pi r^2 \Psi^2 = r^2 R(r)^2$$

-1s:

$$P(r) = \frac{4Z^3}{a_0^3} \cdot r^2 \cdot e^{-2Zr/a_0}, \quad P(0)=0, \quad P(r\to\infty)\to 0$$

$$\frac{dP}{dr} = \frac{4Z^3}{a_0}\left(2r - \frac{2Zr^2}{a_0}\right) e^{-2Zr/a_0} = 0 \Rightarrow r^* = \frac{a_0}{Z}, \quad Z=1 \Rightarrow a_0 = 52.$$

- 2s: $\Rightarrow r^* = 5-2a_0$



(ii) p orbitals

$l = 1 \Rightarrow$ angular momentum magnitude $\sqrt{2}\hbar$

→ At nucleus ($r = 0$) $\Rightarrow \Psi = 0$

-2p, $l = 0 \Rightarrow m_l = -1, \overset{\downarrow}{0}, 1$

zero angular momentum around z-axis

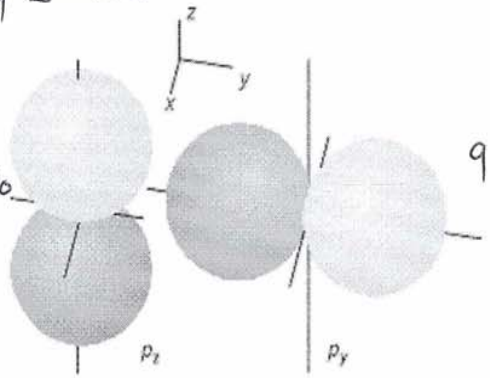
$n = 2, l = 1, m_l = 0$

$$P_0 = R_{2,1}(r)Y_{1,0}(\theta, \phi) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta \cdot e^{-Zr/2a_0}$$

$$= r\cos\theta \cdot f(r)$$

$z = r\cos\theta$

$\therefore p_z = z f(r)$: p_z orbital



9 pm

$n = 2, l = 1, m_l = \pm 1$

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

$$= \mp\frac{1}{2^{1/2}} \cdot r\sin\theta\, e^{\pm i\phi} \cdot f(r)$$

$e^{+i\phi}$: clockwise (angular momentum) around z-axis

$e^{-i\phi}$: counter-clockwise ''

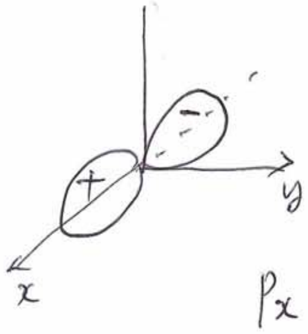
→ imaginary ⇒ take the real linear combinations

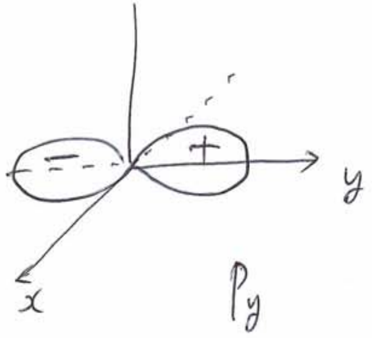
e.g.

$(e^{i\phi} + e^{-i\phi} = 2\cos\phi,$

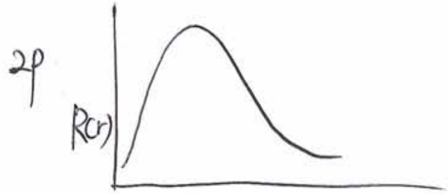
$$p_x = -\frac{1}{2^{1/2}}\left(p_{+1} + p_{-1}\right) \simeq r\sin\theta\cos\phi\, f(r) = x f(r)$$

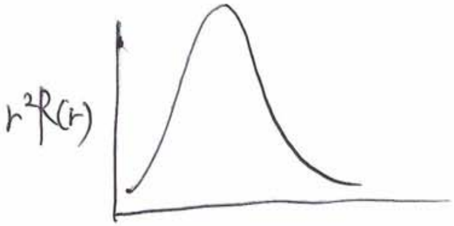
$$p_y = \frac{i}{2^{1/2}}\left(p_{+} - p_{-1}\right) \simeq r\sin\theta\sin\phi\, f(r) = y f(r)$$

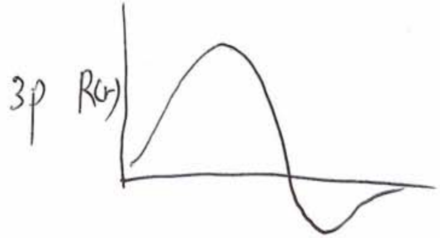


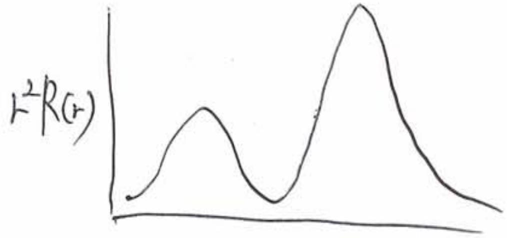


no net angular momentum around z-axis









(iii) d orbitals

$n = 3, l = 0, 1, 2 \qquad l = 2 \Rightarrow m_l = -2, -1, 0, +1, +2$

$$d_{xz} = \frac{1}{\sqrt{2}}\left(d_{+1} + d_{-1}\right) = xz f(r)$$

$$d_{yz} = \frac{1}{\sqrt{2}\,i}\left(d_{+1} - d_{-1}\right) = yz f(r)$$

$$d_{xy} = \frac{1}{\sqrt{2}}\left(d_{+2} + d_{-2}\right) = xy f(r)$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}\,i}\left(d_{+2} + d_{-2}\right) = \frac{1}{2}(x^2-y^2) f(r)$$

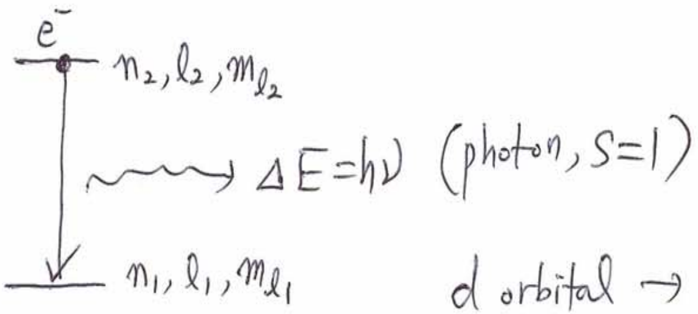
$$d_{z^2} = d_0 = \frac{1}{2\sqrt{3}}\left(3z^2 - r^2\right) f(r)$$

(4) Selection rule ⇒ spectroscopic transitions

- all possible transitions ((n, l, m_l) are not permissible

(why? Photons has an intrinsic spin angular momentum of s =1 (m_s = 0, ± 1))

↑ spin magnetic q. #.



d orbital ($l=2$) → s orbital ($l=0$) (X) ∵ photon cannot carry away enough angular momentum ($\Delta l = 2$)

s → s (X)

∵ no angular momentum for photon ($\Delta l = 0$)

- allowed vs. forbidden transition

- Selection rule for allowed transition

(n can be any value since n is not relate directly to the angular momentum)

Lyman series (UV) from p (2p, 3p…) to 1s

Balmer (visible)

$E \propto Z^2$, 1s He^+ size = ½(1s H)

< SUMMARY> : Hydrogenic atoms: one electron

- Schrödinger equation → n, l, m_l

$$\begin{array}{ccc} n, & l, & m_l \\ \downarrow & \downarrow & \downarrow \\ 1 & s & p_x, p_y, p_z \\ 2 & p & \vdots \\ \vdots & d & \\ & \vdots & \text{degenerate} \end{array}$$

- each electron orbital is doubly degenerate : spin

$$\Rightarrow m_s = \pm\frac{1}{2}$$

- Spectroscopy ← selection rule (∵ photon $S=1$)

$$\Delta l = \pm 1, \quad \Delta m_l = 0 \ \text{or} \ \pm 1$$

Atomic Structure: Many-electron atoms

rinciples of quantum mechanics → <u>internal structure of atoms</u>

1. Hydrogenic atom: one electron atom or ion
2. <u>Many electron atom</u>: complicated but same principle
3. Atomic spectroscopy: experimental technique to determine the electronic structure of atoms

1. Many electron atoms

- complicated since electrons interact with one another ⇒ "approximation"

(1) Orbital approximation

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots)$, $\mathbf{r}_i$: vector from nucleus to electron i

Orbital approximation: $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots) = \Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2)\Psi(\mathbf{r}_3)\ldots..$

⇒ exact if there were no interactions between electrons

1) He

i) Simple approach: structure of hydrogenic atoms many electron atoms

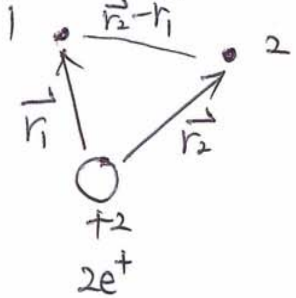
ii) Numerical computations

Hydrogenic atom (ground state) $1s^1$ "configuration"

(single electron in 1s orbital)

He (2 electrons) → $1s^2$

$Z = 2$, nucleus charge $2e^+$: more compact orbital than H



$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{H}\psi = E\psi$$

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)$$

$$\hat{V} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}}\right), \quad r_{12} = |\vec{r_2} - \vec{r_1}|$$

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{2}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{2}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}$$

r_{12} : not fixed at each moment

Assume that $\frac{1}{r_{12}} = 0$

$\psi = \psi(r_1)\psi(r_2)$, $E = E_1 + E_2$ → approximation → "configuration"

(list of occupied orbitals)

Actually, $\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|r_1 - r_2|}$

2) Li

He: $1s^2$
Li, $Z = 3$, 3 electrons $1s^3$?

- Pauli exclusion principle (1924)

"No more than two electrons may occupy and given orbital and, if two do occupy one orbital, then their spins must be paired" (special case of Pauli principle)

"When the labels of any two identical fermions are exchanged, the total wavefunction changes sign"

(fermions: particle with half integer, spin boson: same sign)

→ No two electrons in a given atom can have all four quantum numbers (n, l, m_l, m_s) the same

→ A wavefunction for a system of electrons must be antisymmetric for exchange of any pair of electrons

Two e^- $\psi(1,2)$

$\Rightarrow \psi(2,1) = -\psi(1,2)$ $\qquad$ $\psi \longrightarrow -\psi_{n,l,m_l,m_s}$

orbital approximation

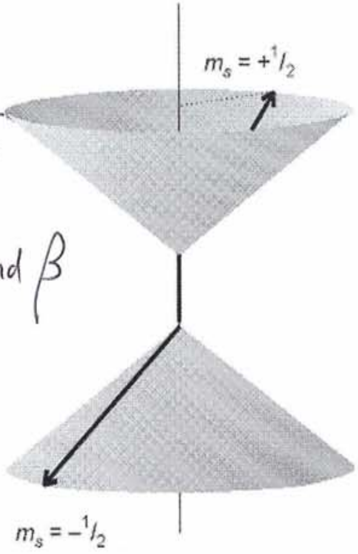
$\psi(1,2) = \psi(1)\psi(2)$

2 Spins : $\alpha(1)\alpha(2)$ $\qquad$ $\alpha : m_s = +\frac{1}{2}$, $\beta : m_s = -\frac{1}{2}$

$\beta(1)\beta(2)$

$\alpha(1)\beta(2)$, $\beta(1)\alpha(2)$ → cannot tell which e^- is α and β

↳ normalized linear combination



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

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

Wavefunction ψ

$\psi(1)\psi(2)\alpha(1)\alpha(2)$, $\psi(1)\psi(2)\beta(1)\beta(2)$, $\psi(1)\psi(2)\sigma_+(1,2)$, $\psi(1)\psi(2)\sigma_-(1,2)$

- $\psi(1)\psi(2)\alpha(1)\alpha(2)$ ↓ not allowed ($\because$ do not change sign)
- $\psi(1)\psi(2)\beta(1)\beta(2)$ ↓ not allowed
- $\psi(1)\psi(2)\sigma_+(1,2)$ ↓ not allowed ($\because \sigma_+(2,1) = \sigma_+(1,2)$)
- $\psi(1)\psi(2)\sigma_-(1,2)$ ↓ "allowed" ($\sigma_-(2,1) = -\sigma_-(1,2)$)

$\Rightarrow$ Only paired α and β spins allowed

$\uparrow\downarrow$: zero net spin angular momentum ($m_s = +\frac{1}{2}$, $m_s = -\frac{1}{2}$)

Li: K shell (1s) is full → 3^{rd} electron → $2s^1$ or $2p^1$??

- Hydrogenic atoms, 2s, 2p → L shell degenerate

- Many electrons atoms → not degenerate

Electron experiences a Coulombic repulsion from other electrons

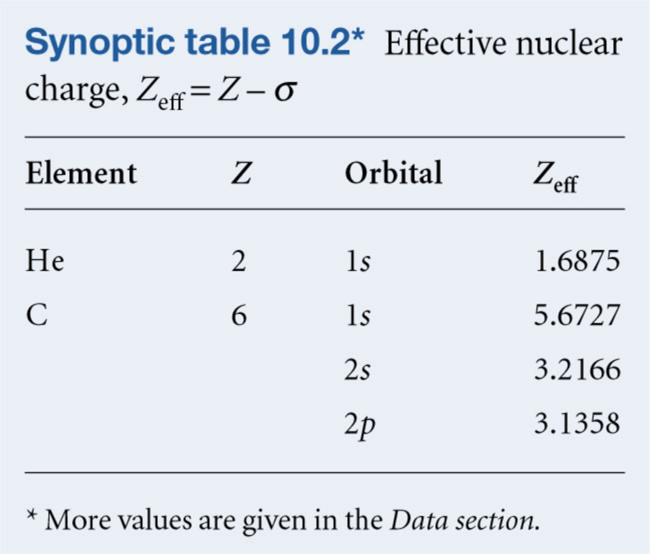
Li: ideal charge $Ze = 3e^-$
→ but 2s electron feels less attractive charge than Ze^- since other electrons in 2s

$$Ze^- \longrightarrow Z_{eff}e^- \quad \text{(effective nuclear charge)}$$

$$Z_{eff} = Z - \sigma \qquad (\sigma : \text{shielding constant (screening constant)}$$

- Shielding constant is different for 2s and 2p since Different radial distribution

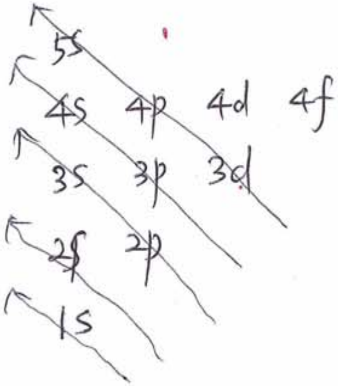
s electron has greater penetration through inner shells
Than a p electron → s: more close to the nucleus
(feel less shielding than p electron)



Synoptic table 10.2* Effective nuclear charge, $Z_{\text{eff}} = Z - \sigma$

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

* More values are given in the *Data section*.



3) The building-up principle (Aufbau principle)

- order of occupation for ground state configuration

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s \cdots$

each orbital up to $2e^-$s

→ Complicated effects from electron-electron repulsion, e.g., 4s, 3d

p subshell → 3 orbitals → $6e^-$

d " → 5 " → $10e^-$

Be : $1s^2 2s^2$, B : $1s^2 2s^2 2p^1$

C (Z=6) : $1s^2 2s^2 2p^2$ or $\overset{1s^2}{[He]} 2s^2 2p^2$

⇓

$2e^-$ to occupy different 2p orbitals because the repel each other ($2p_x$, $2p_y$)

↑ ↑ — (o), ⇅ — — (x)

- 2nd rule of building-up principle: "electrons occupy different orbitals of a given subshell before doubly occupying any one of them"

N$(z=7) \rightarrow [He]\ 2s^2 2p_x^1 2p_y^1 2p_z^1$ $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$

O$(Z=8) \rightarrow [He]\ 2s^2 2p^4 \rightarrow [He]\ 2s^2 2p_x^2 2p_y^1 2p_z^1$

Why $\underline{\uparrow}\ \underline{\uparrow} < \underline{\uparrow\downarrow}\ \underline{\ \ }$

lower energy

parallel → e^--nucleus interaction is improved

↳ stay well apart → less interaction → repel each other less

- Hund's rule: " an atom in its ground state adopts a configuration with the greatest number of unpaired electrons"

$[Ne](z=10) \rightarrow [He]\ 2s^2 2p^6 \equiv [Ne]$

Na$(Z=11) \rightarrow [Ne]\ 3s^1$

→ chemical periodicity

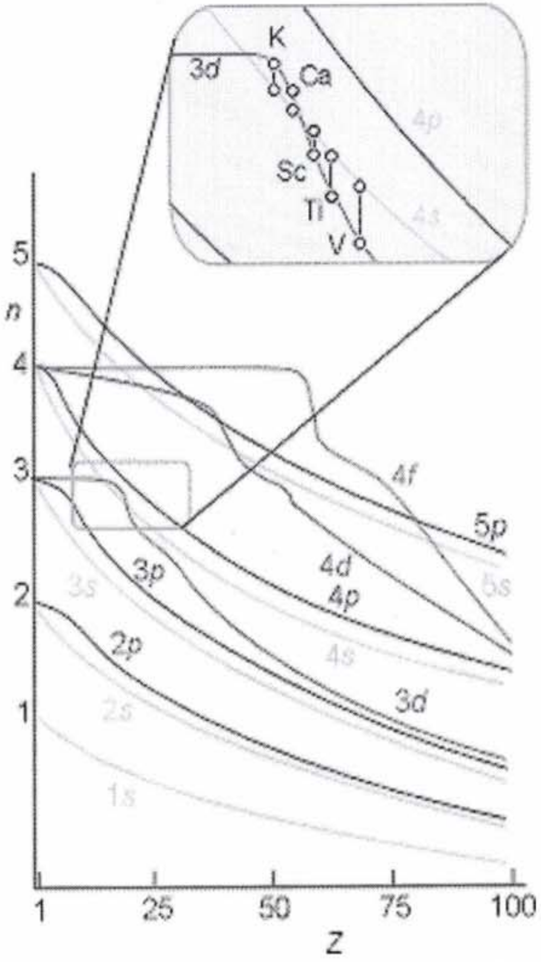
K $n=1 \rightarrow 2e^-$

L $n=2 \rightarrow 8e^-$

Ca$(Z=20)$ $[Ar]4s^2$

3d : Sc → Zn : 5 - 3d orbitals

⇒ less clear since $e^- - e^-$ repulsions
$(d-d)$, $(4s-3d)$



4) Configurations of ions

Fe → $[Ar]3d^6 4s^2$

$Fe^{3+} \rightarrow [Ar]3d^5$

O → $[He]2s^2 2p^4$

$O^{2-} \rightarrow [He]2s^2 2p^6$

(2) Self-consistent field orbitals (SCF) (p.344 (7판 p.392))

- Hartree-Fock method: opportunity for calculating the energies of many electron systems
- electron-electron interaction term: difficulty of Schroeginger equation

Potential energy of the electron

$$V = -\sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \boxed{\frac{1}{2}} {\sum_{ij}}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad i \neq j$$

$\downarrow$ total attractive interaction between e^-s and nucleus

$\downarrow$ e_1 with e^2 $= e_2$ with e_1

$\downarrow$ total repulsive interaction r_{ij} ; distance e^- i and j

→ Computational technique for the numerical solutions for the wavefunctions and energies

- approximate form → orbital → repeat calculation → improved orbital → recycle until insignificantly different stating orbitals and energies

⇒ self-consistent orbital

$\longrightarrow$ show periodicities

Li : low I_1 $Z = 3 \longrightarrow Z_{eff} = 1.3$, easy to remove, $[He]2s^1$

Be : higher nuclear charge than Li $\longrightarrow$ more difficult to remove outermost electron, $[He]2s^2$

B : $[He]2s^2 2p^1$ 2p electron is less strongly bound than 2s electron
C : increased since nuclear charge has increased
N: increased since nuclear charge has increased, $[He]2s^2 2p^3$

O: $[He]2s^2 2p^4$ doubly occupied $\longrightarrow$ electron-electron repulsion
$\longrightarrow$ easy to remove

F : increase, higher nucleus charge
Ne : $[He]2s^2 2p^6$
Na : $[Ne]3s^1$, far from the nucleus, nuclear charge is shielded by the neon-like core (K_1 L shell) $\longrightarrow$ lower I_1

K: $[Ar]4s^1$

(2) Self-consistent field orbitals (SCF) (p.344 (7판 p.392))

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$$V = -\sum_{i} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \boxed{\frac{1}{2}} \sum_{ij}{}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \qquad i \neq j$$

↓ total attractive interaction between e^-s and nucleus

↓ e_1 with e^2 = e_2 with e_1

↓ total repulsive interaction

r_{ij} ; distance e^- i and j

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⇒ self-consistent orbital

Atomic Structure: spectra of complex atoms

The principles of quantum mechanics → internal structure of atoms

1. Hydrogenic atom: one electron atom or ion

2. Many electron atom: complicated but same principle

3. Atomic spectroscopy: experimental technique to determine the electronic structure of atoms

- Frequency $\nu = |\Delta E|/h$ or wavenumber $\nu = |\Delta E|/hc$

- actual energy levels are not given solely by the energies of the orbitals due to electrons interact with one another in various ways
- high resolution → fine structure: i) singlet or triplet
  ii) spin-orbit interaction

(1) Singlet and triplet states

He atoms: $1s^2$
Excited state: $1s^2 \rightarrow 1s^1 2s^1$

$1s^1 2s^1$: parallel < antiparallel
triplet < singlet
(lower E) → the effect of spin correlation on the Coulombic interaction between electrons

He: difference between triplet < singlet

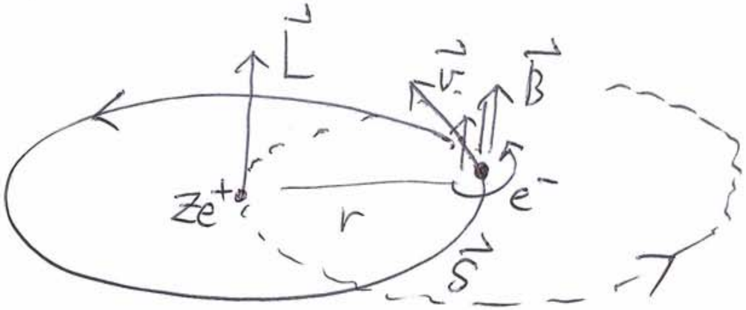
6421 cm^{-1} (0.7961 eV)

No transition betwn singlet & triplet levels: light does not affect the spin directly

→ the relative orientation of two electrons spins cannot change during a transition

(2) Spin-orbit coupling

Magnetic moment between the spin and orbital angular momentum



e^{-} feels magnetic moment.

spin angular momentum → magnetic moment
(∵ moving charge generate magnetic field)

orbital angular momentum → magnetic moment
($l > 0$) (∵ circulating)

⇒ interaction spin and orbital magnetic moments → "spin-orbit coupling"

$$\vec{B} = \left(\frac{\mu_0 Ze}{4\pi} \cdot \frac{1}{mr^3}\right)\vec{L} \quad , \quad \vec{\mu}_s = -\frac{e}{m}\vec{S}$$

Coupling energy

$$E_{s,o} = -\vec{\mu}_s \cdot \vec{B} = -\left(\frac{e}{m}\right)\vec{S} \cdot \left(\frac{\mu_0 Ze}{4\pi} \cdot \frac{1}{mr^3}\right)\vec{L} = \xi(r)\,\vec{L} \cdot \vec{S}$$

Total angular momentum (*j*)

$j = l+s,\ l+s-1, \cdots |l-s| \quad j \geq 0$

↓

Same directn
(spin & orbital)

↓

parallel

↓

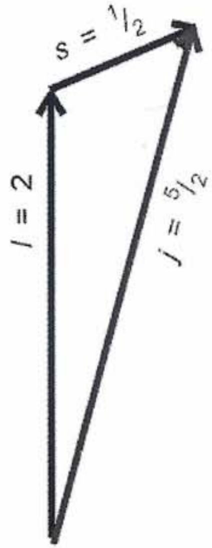
high total angular momentum

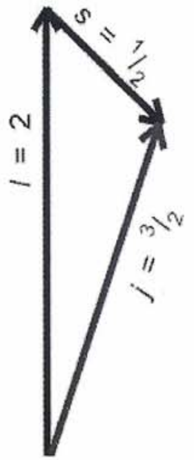
$j = l + \frac{1}{2}\ ,\ l - \frac{1}{2}$ (opposite)

For $l=0 \Rightarrow j = \frac{1}{2}$ only

$l=1 \Rightarrow j = \frac{3}{2}$ or $\frac{1}{2}$

$l=2 \Rightarrow$ ~~j~~ $j = \frac{5}{2}, \frac{3}{2}$ d electrn





$$\vec{j}^{\,2} = \vec{j}\cdot\vec{j} = (\vec{\ell}+\vec{s})\cdot(\vec{\ell}+\vec{s}) = \vec{\ell}^{\,2} + \vec{s}^{\,2} + 2\vec{\ell}\cdot\vec{s}$$

$$\vec{\ell}\cdot\vec{s} = \frac{1}{2}\left(\vec{j}^{\,2} - \vec{\ell}^{\,2} - \vec{s}^{\,2}\right)$$

C.M → operator

$$\hat{\ell}\cdot\vec{s} = \frac{1}{2}\left(\hat{j}^{2} - \hat{\ell}^{2} - \hat{s}^{2}\right)$$

ψ → eigenvalue

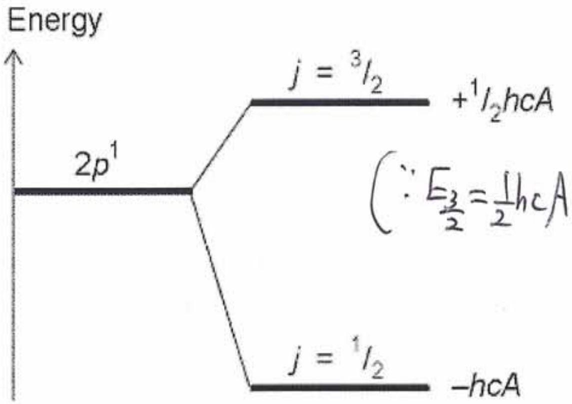
$$E_{s,o} = \xi(r)\cdot\frac{1}{2}\hbar\left\{j(j+1) - \ell(\ell+1) - s(s+1)\right\}$$

∴ Energy with quantum number s, ℓ, j

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

↓

spin-orbit coupling constant
(cm^{-1} unit)

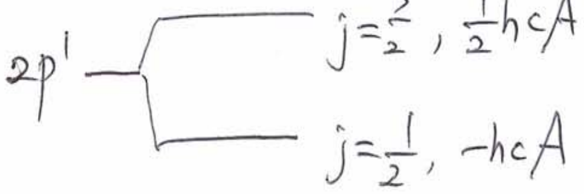


$$\left(\because E_{\frac{3}{2}} = \frac{1}{2}hcA\left\{\frac{3}{2}\times\frac{5}{2} - 1\times2 - \frac{1}{2}\times\frac{3}{2}\right\}\right)$$

$$\left(\because E_{\frac{1}{2}} = \frac{1}{2}hcA\left\{\frac{1}{2}\times\frac{3}{2} - 1\times2 - \frac{1}{2}\times\frac{3}{2}\right\}\right)$$

e.g.) $H: 1s^1 \rightarrow j = l+s,\ l+s-1,\ \cdots |l-s| = \frac{1}{2}$

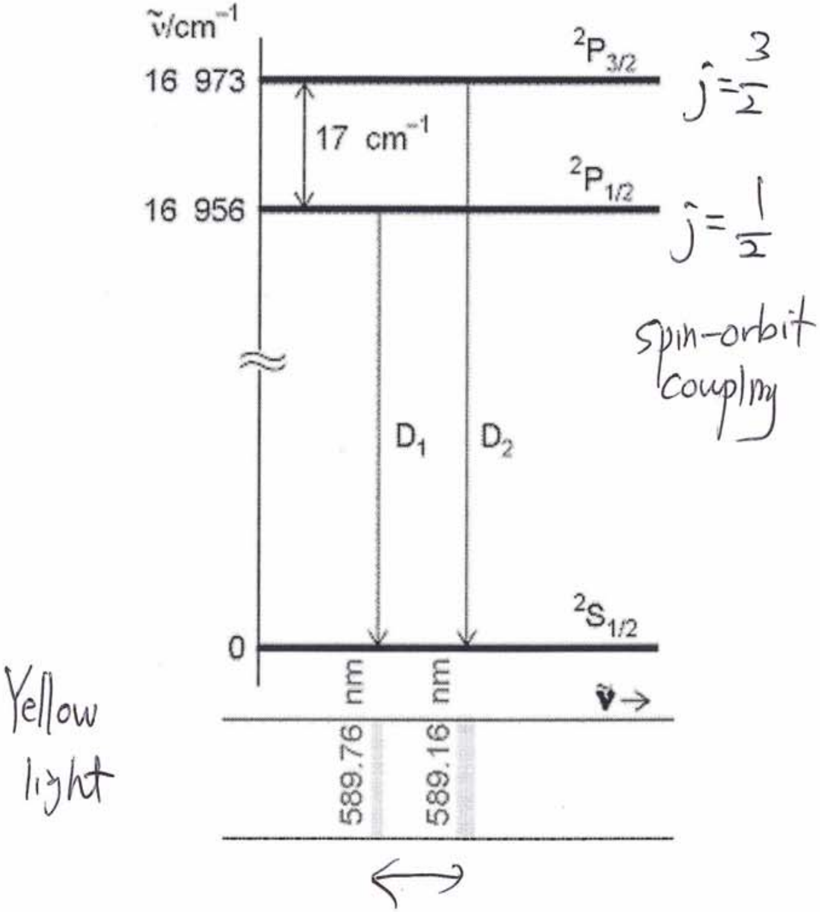
p-electron
$(l=1, s=\frac{1}{2}) \Rightarrow j = \frac{3}{2}$ and $\frac{1}{2}$



nuclear charge ↑ → coupling ↑

$Na: 1s^2 2s^2 2p^6 3s^1\ :\ 3p \rightarrow 3s$

$\Delta\nu = \frac{3}{2}A \Rightarrow A = 11.5\ cm^{-1}$



(3) Term symbols (for atoms)

↳ Convey all information much more succinctly

e.g.) $^2P_{3/2}$, $^3D_1$

$$\Rightarrow \boxed{\;^{2S+1}L_J\;}$$

i) L : total orbital angular momentum quantum number

$L = l_1+l_2,\ l_1+l_2-1, \cdots |l_1-l_2|$ non-negative

- Consider unfilled shell only (Closed shell : zero orbital ang. mom.)

e.g.) $[Ne]3s^1 \rightarrow S$

$F: [He]2s^2 2p^5 \rightarrow$ one $p\ e^-$ unfilled $\rightarrow P$

$$\begin{array}{cccccc} L: & 0, & 1, & 2, & 3, & 4 \cdots \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ & S & P & D & F & G \cdots \end{array}$$

e.g.) $2p$ e^-s, $l_1 = l_2 = 1 \Rightarrow L = 2, 1, 0 \Rightarrow D, P, S$ terms

$d^2 \rightarrow L = 4, 3, 2, 1, 0 \Rightarrow G, F, D, P, S$

$$p^3 \rightarrow L_1 = 2, 1, 0 \Rightarrow L_2 : \begin{array}{l} 3, 2, 1 \\ 2, 1, 0 \end{array} \Rightarrow 1F, 2D, 3P, 1S$$

ii) $2S+1$: multiplicity : singlet or triplet

S: total spin angular momentum quantum number

$$S = s_1 + s_2,\ s_1 + s_2 - 1, \cdots |s_1 - s_2|$$

$2e^-$: $s = \frac{1}{2} \Rightarrow S = 1, 0$

$3e^- \rightarrow S = \frac{3}{2}, \frac{1}{2}$ and $S = \frac{1}{2}$

When $S = 0 \rightarrow e^-$ are all paired, no net spin → singlet

$\rightarrow$ multiplicity $= 2S + 1 = 1$ e.g.) ${}^1S$

- single e^- : $s = \frac{1}{2} \Rightarrow S = \frac{1}{2} \Rightarrow 2S+1 = \boxed{2}$

  e.g.) $[Ne]3s^1 \Rightarrow {}^2S$, $[Ne]3p^1 \Rightarrow {}^2P$

- singlet (e^- paired) : $2e^-$ case $\Rightarrow S=0$ $(\frac{1}{2}, -\frac{1}{2}) \Rightarrow 2S+1 = \boxed{1}$
- triplet (e^- unpaired) : $2e^-$ case $\Rightarrow S=1$ $(\frac{1}{2}, \frac{1}{2}) \Rightarrow 2S+1 = \boxed{3}$

(iii) J : total angular momentum quantum number ← spin-orbit interaction

j : relative orientation of spin and orbital angular momentum

ⓐ $1e^-$ (outside a closed shell)

$J = j \Rightarrow l + \frac{1}{2}, |l - \frac{1}{2}|$

$[Ne]\,3s^1$, $l=0$, $s=\frac{1}{2} \Rightarrow j = \frac{1}{2}$, ${}^2S_{1/2}$

$[Ne]\,3p^1$, $l=1 \Rightarrow j = \frac{3}{2}, \frac{1}{2} \Rightarrow {}^2P_{3/2}$ and ${}^2P_{1/2}$

ⓑ many e^- atoms → two ways

①

$$\left.\begin{array}{l} l_1 \quad l_2 \quad l_3 \quad l_4 \cdots \Rightarrow L = l_1 + l_2 \cdots \\ s_1 \quad s_2 \quad s_3 \quad s_4 \cdots \Rightarrow S = \cdots\cdots \end{array}\right\} \Rightarrow J = L+S,\ L+S-1, \cdots |L-S|$$

$$\begin{array}{lll} \Downarrow & \Downarrow & \Downarrow \\ \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \cdots \end{array}$$

② $\underbrace{\hat{j}_1 \quad \hat{j}_2}$

$$J = j_1 + j_2 \cdots\cdots$$

① Russell-Saunders coupling : spin-orbit coupling is weak
($Z \leq 40$)

$$\left.\begin{array}{l} l_1, l_2 \cdots \rightarrow L \\ s_1, s_2 \cdots \rightarrow S \end{array}\right\} \Rightarrow J = L+S,\ L+S-1, \cdots |L-S|$$

e.g.) [Ne] $2p^1 3p^1$, excited $2p^2$ - carbon

$$l_1 = 1,\ l_2 = 1 \Rightarrow L = 2, 1, 0$$

$$s_1 = \frac{1}{2},\ s_2 = \frac{1}{2} \Rightarrow S = 1, 0$$

$\Rightarrow$	^3D	^1D	^3P	^1P	^3S	^1S
	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$
	$L=2$	$L=2$	$L=1$	$L=1$	$L=0$	$L=0$
	$S=1$	$S=0$	$S=1$	$S=0$	$S=1$	$S=0$
	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$	$\Downarrow$
	$J=3,2,1$	$J=2$	$J=2,1,0$	$J=1$	$J=1$	$J=0$
	$^3D_3$ $^3D_2$ $^3D_1$	$^1D_2$	$^3P_2$ $^3P_1$ $^3P_0$	$^1P_1$	$^3S_1$	$^1S_0$

② jj-coupling : spin-orbit coupling is large
($Z > 40$)

l_1 l_2 ..
s_1 s_2 ..
$\Downarrow$ $\Downarrow$
j_1 $j_2 \cdots \Rightarrow J = j_1 + j_2, \cdots |j_1 - j_2|$

e.g.) p^2 in heavy atom ($Z > 40$), $l_1 = 1, s_1 = \frac{1}{2} \Rightarrow j_1 = \frac{3}{2}, \frac{1}{2}$
$l_2 = 1, s_2 = \frac{1}{2} \Rightarrow j_2 = \frac{3}{2}, \frac{1}{2}$.

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

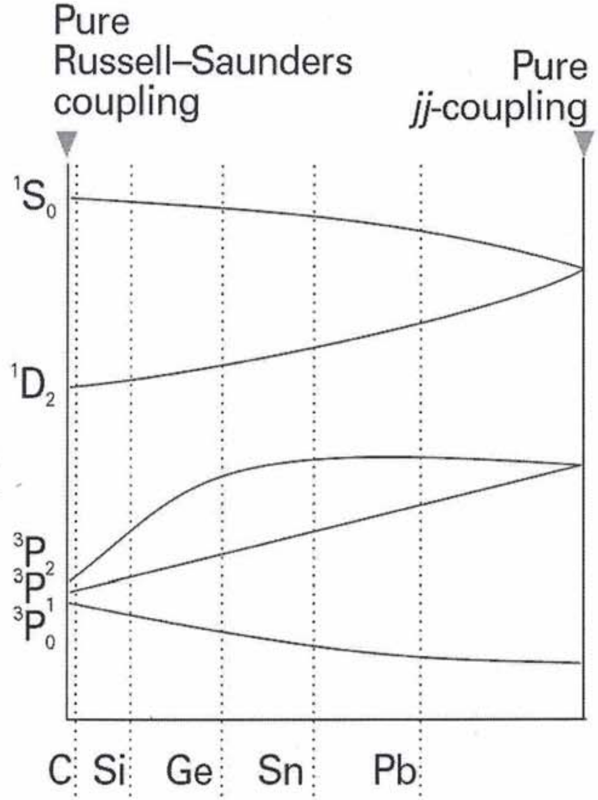


Fig. 10.34 The correlation diagram for some of the states of a two-electron system. All atoms lie between the two extremes, but the heavier the atom, the closer it lies to the pure *jj*-coupling case.

(5) Selection rule

∵ photon : spin of 1 $(S = 1 ,\ m_s = 0, \pm 1)$

↑ Spin ang. mom. q. #

→ fail in heavy atom since jj-coupling

- One e^- atom

$$\Delta n = \text{any value}$$
$$\Delta l = \pm 1$$
$$\Delta m = 0, \pm 1$$

- many e^- atoms

$$\Delta S = 0$$
$$\Delta L = 0, \pm 1,\ \Delta l = \pm 1$$
$$\Delta J = \pm 1, 0,\ \text{but } J = 0 \not\leftrightarrow J = 0$$

Singlet ↔ triplet transition forbidden (no change of overall spin)

∵ light does not affect the spin directly

the relative orientation of two e^- spins cannot change during a transition