Atomic Structure 1: Hydrogenic Atom

Reading: Atkins, Ch. 10

The principles of quantum mechanics → internal structure of atoms

1. **Hydrogenic atom**: one electron atom or ion (e.g., H, He^{+}, Li^{2+}, U^{91+})

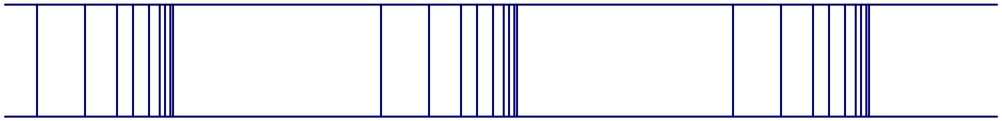
→ Schrödinger equations can be solved exactly

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)

$n_2 = n_1 + 1, n_1 + 2 \ldots\ldots$

$h\nu = E_2 - E_1$ "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

- internal motion of electron relative to the nucleus :

relative motion of electron and nucleus

Schrödinger equation, $H\Psi = E\Psi$

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

Multiply r^2/RY,

Y: angular variables $\longrightarrow$ constant

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

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

$V_{eff} =$

↓ 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
→ repulsion
$r =$: similar to $l = 0$

Radial equation

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

$E_n =$

Ψ = RY

n = 1, l = 0, m_l = 0, $\Psi_{100}(r, \theta, \phi) = R_{10}(r)Y0_0(\theta, \phi) =$

3 quantum numbers
n = 1, 2, 3……….
l = 0, 1, 2, 3……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) <u>Principle quantum number</u> (n), n = 1,2,3…..

⇒ Determine the energy of the electron

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

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

iii) <u>Magnetic quantum number</u> (m_l), $m_l = 0, \pm 1, \pm 2, \pm 3, \ldots.$

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

iv) <u>Spin magnetic quantum number</u> (m_s)

⇒ Intrinsic angular momentum by two quantum numbers s,

$$s = ½, m_s = \pm ½$$

$E_n =$

Shell, n = 1, 2, 3, 4, …..
K L M N

Subshell *l* = 0, 1, 2, 3, 4, ….
s p d f g h I

(i) s orbitals

- n =1, l = 0, m_l = 0 (<u>1s</u>)

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

⇒ Independent of angle, same value
at all points of constant radius

Probability at $r = 0 \Rightarrow$

All s orbitals ⇒ spherically symmetric,
but differ in number of radial nodes

- <u>2s</u>: n = 2, l = 0, m_l = 0

$$\Psi_{2s} =$$

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

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

  radial distribution function

  $P(r) =$

-<u>1s</u>:

P(r) =

- <u>2s</u>:

(ii) p orbitals

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

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

-2p, $l = 0 \Rightarrow m_l = -1, 0, 1$

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

$P_0 = R_{2,1}(r)Y_{1,0,0}\,(\theta, \phi) =$

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

$P_{\pm 1} = R_{2,1}(r)Y_{1,\,\pm 1}\,(\theta, \phi) =$

(iii) d orbitals

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

(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 ($m_s = 0, \pm 1$))

- allowed vs. forbidden transition

- Selection rule for alloed transition

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

Lyman series (UV)

Balmer (visible)

< SUMMARY> : Hydrogenic atoms: one electron

Atomic Structure 2: Many-electron atoms

Reading: Atkins, ch. 13
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

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) $\longrightarrow$ $1s^2$

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

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

Li: K shell (1s) is full ⟶ 3rd 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

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

$Z_{eff} = Z - \sigma$ (σ : 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)

3) The building-up principle (Aufbau principle)
- order of occupation for ground state configuration

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

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

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

4) Configurations of ions

5) Ionization energies and electron affinities

- 1st ionization energy (I_1): minimum energy necessary to remove an electron from a many electron atoms
- 2nd ionization (I_2): minimum energy necessary to remove 2nd electron from a many electron atoms

- Electron affinity (E_{ea}) : the energy released when an electron attaches to a gas-phase atom

e.g., $Cl \rightarrow Cl^-$

→ 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 → more difficult to remove outermost electron, $[He]2s^2$

B : $[He]2s^22p^1$ 2p electron is less strongly bound than 2s electron
C : increased since nuclear charge has increased
N: increased since nuclear charge has increased, $[He]2s^22p^3$

O: $[He]2s^22p^4$ doubly occupied → electron-electron repulsion
→ easy to remove

F : increase, higher nucleus charge
Ne : $[He]2s^22p^6$
Na : $[Ne]3s^1$, far from the nucleus, nuclear charge is shielded by the neon-like core (K_1 L shell) → lower I_1

K: $[Ar]4s^1$

(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

→ 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

Atomic Structure 3: spectra of complex atoms

Reading: Atkins, ch. 10 (7판 ch. 13)

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1. Hydrogenic atom: one electron atom or ion
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3. Atomic spectroscopy: experimental technique to determine the electronic structure of atoms

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

- 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) <u>singlet or triplet</u>
  ii) <u>spin-orbit interaction</u>

(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

$6421\ \mathrm{cm}^{-1}$ (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

Total angular momentum (*j*)

(3) Term symbols (for atoms)

(5) Selection rule