Electronic structure

- Structure of an atom
- Electron orbitals and energy

Quantum state of an electron - Quantum numbers

3 spatial coordinates

$n$ Principal (shell) 1, 2, 3, ...
radial = size K, L, M...

$l$ Orbital – angular momentum
(subshell) 0 to $n$-1
s (sharp) $\ell = 0$
p (principal) $\ell = 1$
d (diffuse) $\ell = 2$
f (fundamental) $\ell = 3$

$m_l$ Orbital – Orientation (Magnetic, energy shift, or energy level for each subshell)

Orientation: $l$ to $-l$
Example: for $l = 2$, $m_l = -2, -1, 0, 1, 2$
Quantum state of an electron - Quantum numbers

$m_s$ Spin $\frac{1}{2}$, $-\frac{1}{2}$

Single electron state of motion… $n$, $\ell$, $m$, $m_s$

$j$ Total angular momentum (quantum number $j$)

$\ell \pm \frac{1}{2} = \ell + m_s$

(except $\ell = 0$, where $j = \frac{1}{2}$ only)

The Orbitron

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http://winter.group.shef.ac.uk/orbitron
Quantum Numbers for Electrons in Atomic Electron Shells

<table>
<thead>
<tr>
<th>X-ray notation</th>
<th>Modern notation</th>
<th>n</th>
<th>\ell</th>
<th>j = \ell + m_\ell</th>
<th>(2j + 1)</th>
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<tbody>
<tr>
<td>K</td>
<td>1s</td>
<td>1</td>
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<tr>
<td>L_\text{I}</td>
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<td>2</td>
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<tr>
<td>L_\text{II}</td>
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<td>2</td>
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<td>N_\text{VII}</td>
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<td>3</td>
<td>3½</td>
<td>8</td>
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Energy (or wavelength) of an X-ray depends on
Which shell ionization took place
Which shell relaxation electron comes from

Siegbahn notation...

- K radiation
  
  Electron removed from K shell

  \( K_a \) electron fills K hole from L shell

  \( K_\beta \) electron fills K hole from M shell

- L radiation

  Electron removed from L shell

  \( L_a \) electron fills L hole from M shell

  \( L_\beta \) electron fills L hole from M or N shell

  Depends on which \( \beta \) transition – which L level ionized and which M or N level is the source of the de-excitation electron
Energy level representation of characteristic X-ray emission process

Vacuum

Valence level

M...

Kα

\( L_{\text{II}} \) (2p\(^{3/2}\))

\( L_{\text{I}} \) (2p\(^{1/2}\))

\( L_1 \) (2s)

\( K \) (1s)

Sufficiently energetic beam electron ionizes K shell...

\( L_1 \) (2s) → \( K \) (1s), why not?

Selection rules for allowed transitions involving photon emission

**Conservation of angular momentum**

1. Change in \( n \) (principal) must be \( \geq 1 \)
2. Change in \( \ell \) (subshell) can only be +1 or -1
3. Change in \( j \) (total angular momentum) can only be +1, -1, or 0

The photon, following Bose-Einstein statistics, has an intrinsic angular momentum (spin) of 1.

A K-shell vacancy (\( \ell = 0 \)) must be filled by an electron from a p-orbital, but can be 2p (L-shell; \( \ell = \pm 1 \)), 3p (M-shell; \( \ell = \pm 1 \)), or 4p (N-shell \( \ell = \pm 1 \))

So can’t fill \( K \) from \( L_1 \) (2s) in transitions involving photon emission
Example of scandium (Sc) – 21 electrons

Rule 1) no transitions between shells in same row
Rule 2) no transitions between shells in the same column or that skip columns (e.g., from $\ell = 3$ to $\ell = 1$)

$\Rightarrow$ Transition NOT possible!

Rule 3) need to check if $\Delta j = 0$ or $\pm 1$

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$s$</th>
<th>$j$</th>
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<th>$s$</th>
<th>$j$</th>
<th>$\Delta j$</th>
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<td>½</td>
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etc...

X-ray lines and electron transitions

Normal (diagram) level

Energy level (core or valence) described by the removal of a single electron from ground state configuration.

Diagram lines

Originate from allowed transitions between diagram levels.

Non-diagram (satellite) lines

Generally originate from multiply-ionized states

Two vacancies of one shell (e.g. two K ionizations) $\Rightarrow$ hypersatellite

Other effects:

- Auger effect
- Coster-Kronig (subshell) transitions
Energy of an X-Ray

Bohr’s Three Postulates:

1) There are certain orbits in which the electron is stable and does not radiate
- The energy of an electron in an orbit can be calculated;
- That energy is directly proportional to the distance from the nucleus.

_Bohr simply forbids electrons from occupying just any orbit around the nucleus such that they can’t lose energy and spiral in…_

2) When an electron falls from an outer orbit to an inner orbit, it loses energy. This energy loss is expressed as a quantum of electromagnetic radiation

2) A relationship exists between the mass, velocity and distance from the nucleus of an electron and Planck’s quantum constant.

Approximate expression for the energy of the $K\alpha$ X-ray

*(Bohr’s early quantum theory)*

$$
\Delta E \approx \frac{3}{4} \left( \frac{1}{4\pi\varepsilon_0} \right)^2 \frac{me^4}{2\hbar} (Z - 1)^2
$$

- $\varepsilon_0$ = permittivity constant
- $m$ = mass of electron
- $e$ = charge
- $\hbar$ = modified Planck’s constant (= $h/2\pi$)
- $Z$ = atomic number

...or about $\Delta E_{K\alpha} = (10.2 \text{ eV})(Z-1)^2$

So:
- O = 0.5 keV
- Si = 1.7 keV
- Ca = 3.7 keV
- Fe = 6.4 keV
Moseley’s Law

X-Ray energy is related to Z with empirical relationship:

\[ E = A(Z-C)^2 \]

(A and C are constants)

Bohr theory prediction for K\textsubscript{α}… \[ E [\text{eV}] = (10.2)(Z-1)^2 \]

Orbital energies

Order of Orbital Filling

1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 6s, 6p, 6d, 6f, 7s, 7p
Bohr quantized the atom...
• An atom has a set of energy levels
• Some (but not all) occupied by electrons

Not really dealing with isolated atoms, but 3D solids
• As atoms approach each other, each affects the other
• Energy levels are altered, splitting into bands
• Each atom in the system produces another energy level in the band structure
Quantum state of an electron - Quantum numbers

Polar coordinates...

Space geometry of the solution of the Schrödinger equation for the hydrogen atom...

\[ \Psi(n, \theta, \phi) = R(r)P(\theta)F(\phi) \]

- **n** Radial component
  - Principal quantum number
- **l** Colatitude
  - Orbital quantum number
- **m_l** Azimuthal
  - Magnetic quantum number

\[ \Rightarrow \text{Yields three equations for three spatial variables} \]