

CM1102

Chemistry – The Central Science

AY2022/23 Semester 1

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Part I

Environment

1 Light

Light is a form of energy that consists of oscillating *electric* and *magnetic* fields, perpendicular to each other.

| $c = \lambda \nu$ | | |
|-------------------|---------------------------------------|----------------|
| | value | unit |
| c | speed of light = 2.9979×10^8 | m/s |
| λ | wavelength | m |
| ν | frequency | s^{-1} or Hz |

1.1 Wave-particle Duality of Light

Due to the wave nature of light, light waves that are *in phase* undergo **constructive interference**.

Light waves that are *out of phase* undergo **destructive interference** — cancelling out each other.

Due to the particle nature of light, when an object is heated, it emits electromagnetic radiation known as **blackbody radiation**.

The wavelength of light emitted changes as the temperature of the object increases.

| $E = h\nu$ | | |
|------------|---|----------------|
| | value | unit |
| E | energy | J |
| h | Planck's constant = 6.626×10^{-34} | J/s |
| ν | frequency | s^{-1} or Hz |

Putting the two equations above together, we can interconvert between *energy*, *frequency*, and *wavelength*.

| $E = \frac{hc}{\lambda}$ | | |
|--------------------------|---|------|
| | value | unit |
| E | energy | J |
| h | Planck's constant = 6.626×10^{-34} | J/s |
| c | speed of light = 2.9979×10^8 | m/s |
| λ | wavelength | m |

1.2 Photoelectric Effect

Electrons can only be ejected from a surface if incoming **photons** transfer sufficient energy to the atoms on the metal surface.

Electron-volt (eV) is the amount of *kinetic energy* gained by a single electron accelerating from rest though an electric potential difference of 1 volt in vacuum.

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

| $h\nu = \Phi + KE_{\max}$ | | |
|---------------------------|--|----------------|
| | value | unit |
| h | Planck's constant = 6.626×10^{-34} | J/s |
| ν | frequency | s^{-1} or Hz |
| Φ | work function of the metal | eV |
| KE_{\max} | maximum kinetic energy of the ejected electron | eV |

Note that KE_{\max} *cannot be negative*, so its minimum value is 0.

1.3 Solar Spectrum

The **electromagnetic spectrum** comprises of, in increasing energy:

1. radio waves,
2. microwaves,
3. infrared,
4. visible,
5. ultraviolet,
6. X-rays,
7. gamma (γ) rays,

White light disperses into a continuous spectrum in the visible spectrum.

However, sunlight is *not continuous* — there are *dark lines* in the **solar spectrum** due to the composition of the sun and the Earth's atmosphere.

1.3.1 Aside: Spectroscopy

The study of the interaction of electromagnetic radiation with matter to obtain information about the identity and structure of substances.

Absorption spectroscopy reveals that a colored object reflects light of that color and absorbs light of the *opposite color*.

1.3.2 Emission Spectrums

Energy can excite electrons of atoms from their **ground state** to an **excited state**.

In the excited state, electrons have higher energy, and when electrons are relaxed to their ground state, their energy is released as light.

Therefore, the dark lines in the solar spectrum occur due to the absorption of energy by the atoms in the sun's atmosphere.

1.3.3 Rydberg Formula

Used to calculate the wavelengths of a spectral line in hydrogenic species, i.e. H, He⁺, Li²⁺, etc.

It generalizes the Balmer series ($n = 2$) for the visible

region, the Lyman series ($n = 1$) for the UV region, and the Paschen series ($n = 3$) for the IR region.

| $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ | | |
|--|---|-----------------|
| | value | unit |
| λ | wavelength of light emitted | m |
| R_H | Rydberg constant = 1.096776×10^7 | m^{-1} |
| n_1 | final electron state (lower energy) $< n_2$ | int |
| n_2 | initial electron state (higher energy) | int |

2 Energy Levels

In the Bohr model, electrons are allowed only in certain circular orbits around the nucleus, which give rise to the **principal quantum numbers** of n .

Therefore, the energy levels in atomic structures are *quantized*, and the energy levels associated with each electron orbit has a fixed value, hence the term **quantized energy level**.

| $E_n = -\frac{2\pi^2 m_e e^4}{n^2 h^2}$ | | |
|---|---|---------|
| | value | unit |
| E_n | energy level | J |
| m_e | electron mass = 9.1094×10^{-31} | kg |
| e | electron charge = 1.602×10^{-19} | C |
| n | principal quantum number | int |
| h | Planck's constant = 6.626×10^{-34} | J · sec |

Since the only variable is n , the equation is generalizable:

| |
|--|
| $E_n \approx -2.18 \times 10^{-18} \left(\frac{1}{n^2} \right) \text{ J}$ |
| $E_n \approx -13.6 \left(\frac{1}{n^2} \right) \text{ eV}$ |

The **ground state** of electrons, $n = 1$, has the lowest energy level and the most stable.

The **excited states** have values of $n > 1$.

The energy required to excite an electron from the ground state to an excited state $\Delta E = E_{\text{final}} - E_{\text{initial}}$ can be determined using the E_n formula above.

If $\Delta E > 0$, this is known as an **absorption** (or excitation) process, going from a lower energy state to a higher energy state.

Conversely, if $\Delta E < 0$, this is known as an **emission** (or relaxation) process, going from a higher energy state to a lower energy state, which releases energy.

The **ionization continuum** occurs as $n \rightarrow \infty$, $E_n \rightarrow 0$, such that energy levels are no longer quantized.

The **ionization energy** is the minimum energy required to remove one electron from a gaseous atom or molecule.

In the case of hydrogen, $\Delta E = E_{\infty} - E_1 = +13.6 \text{ eV}$.

However, this only applies to 1-electron systems, as we otherwise need to account for electron-electron repulsion, which requires taking into account the nuclear charge, Z^2 :

| |
|--|
| $E_n \approx -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$ |
| $E_n \approx -13.6 \left(\frac{Z^2}{n^2} \right) \text{ eV}$ |

3 Atomic Structure

Electrons, and all matter, behave like waves, which can undergo constructive and destructive interference.

| $\lambda = \frac{h}{mv}$ | | |
|--------------------------|---|-------|
| | value | unit |
| λ | De Broglie wavelength | m |
| h | Planck's constant = 6.626×10^{-34} | J/s |
| m | particle mass | kg |
| v | particle velocity | m/sec |

By **Heisenberg's uncertainty principle**, it is impossible to know the precise position of electrons in an atom.

3.1 Quantum Mechanical Model

A **wave equation** describes the behavior of a specific electron in an atom.

The solution to the wave equation is called a **wave function** (ψ), or an **orbital** — the space boundary where there is a 95% chance of finding the electron.

$|\psi|^2$ is proportional to the *probability density* of an electron being found in 3D space.

The position of an electron could be described using *Cartesian coordinates*, using the wave equation $\psi(x, y, z)$.

Alternatively, using *spherical coordinates*, $\psi(r, \theta, \phi)$:

| $\psi(r, \theta, \phi) = \mathbf{R}(r) \times \mathbf{Y}(\theta, \phi)$ | | |
|---|---|------|
| | value | unit |
| $\mathbf{R}(r)$ | radial wave function | — |
| r | distance of the electron from the nucleus | — |
| $\mathbf{Y}(\theta, \phi)$ | angular wave function | — |
| θ | vertical angle perpendicular to the x-y plane | — |
| ϕ | angle on the x-y plane | — |

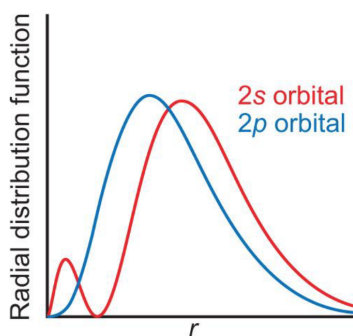
Radial nodes are 3D *spherical* regions where where no electrons are found. The *radial* component of the wave function passes through 0.

Angular nodes are 2D *planar* or 3D *conical* regions where where no electrons are found. The *angular* component of the wave function passes through 0.

In orbital diagrams, the regions corresponding to positive values of the wave function are shaded, while the regions corresponding to negative values are not.

3.1.1 Radial Distribution Function (RDF)

| RDF : $4\pi r^2 \cdot R(r)^2$ | | |
|-------------------------------|--------------------------|------|
| | value | unit |
| $4\pi r^2$ | surface area of a sphere | – |
| $R(r)$ | radial wave function | – |



The maximum value of the RDF (i.e. the peak) is the most probable distance of the electron from the nucleus.

Even though the larger peak of the 2p orbital is closer than that of the 2s orbital, the 2s orbital has a higher energy level than the 2p orbital due to the **penetration** from the smaller peak.

Therefore, within shells of the same quantum number, orbital energy increases as follows: $s < p < d < f$.

Radial nodes can be counted from the x-intercepts, so from the diagram above, the 2s orbital has 1 radial node, while the 2p orbital has none.

3.1.2 Quantum Numbers

| nl_{m_l} , e.g. $2p_z$ | | |
|--------------------------|-----------------------------|------------------------------|
| | value | range |
| n | principal QN | 1, 2, 3, ... |
| l | magnetic QN | 0, 1, ..., $n-1$ |
| m_l | orbital angular momentum QN | $-l, \dots, 0, \dots, +l$ |
| m_s | electron spin QN | $-\frac{1}{2}, +\frac{1}{2}$ |

The principal QN relates to the *size* and *energy* of the orbital — higher principal QNs have larger orbitals with higher energy levels.

The magnetic QN relates to the *shape* of the orbital.

The orbital angular momentum QN relates to the *orientation* of the orbital.

| | |
|-------------------------|-------------|
| number of angular nodes | l |
| number of radial nodes | $n - l - 1$ |
| number of orbitals | $2l + 1$ |

3.2 Electronic Configuration

Pauli's exclusion principle: No two electrons in a given atom can have the exact same set of quantum numbers (n, l, m_l, m_s).

⇒ An atomic orbital has a maximum of 2 electrons of *opposite* spins.

Aufbau principle: Electrons are always placed in the lowest energy sublevel available.

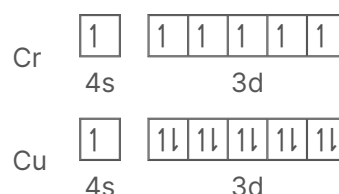
⇒ Fill orbitals starting with the *lowest* energy to get the *ground state*.

Hund's rule: *Degenerate* orbitals are always filled with single electrons before any of them are doubly occupied, and electrons fill separate orbitals with their *spins aligned*.

⇒ Spin-aligned electrons have lower interelectronic repulsion, so the system has less energy.

3.2.1 Exceptions: Cr, Cu

These elements have a lower energy level in these configurations than would typically be expected:



3.3 Trends in Atomic Properties

| trend | → period | ↓ group |
|-------------------|-----------|-----------|
| atomic radius | decreases | increases |
| ionization energy | increases | decreases |
| electron affinity | increases | decreases |

Atomic radius is affected by the **effective nuclear charge** (Z_{eff}) of the atom.

Interelectronic repulsion decreases effective nuclear charge through the **shielding effect** and **penetration**.

Electrons in the inner energy levels have a greater shielding effect than electrons of the same energy level — 2s electrons shield 2p electrons more than other 2p electrons.

| $Z_{\text{eff}} = Z - S$ | | |
|--------------------------|--------------------------------|------|
| | value | unit |
| Z | nuclear charge (atomic number) | int |
| S | shielding constant | real |

Ionization energy is the energy required to remove an electron from a gaseous atom or ion.

Electron affinity is the energy released when an electron is added to a gaseous atom to form an anion.

4 Molecular Structure

A solid object that is heated to high temperatures *emits electromagnetic radiation*.

The wavelength emitted depends on the temperature, by **Wien's displacement law**:

| $\lambda_{\max} = \frac{b}{T}$ | | |
|--------------------------------|--|-------------------|
| | value | unit |
| λ_{\max} | peak wavelength | m |
| b | Wien's displacement constant $\approx 2.898 \times 10^{-3}$ | m K ⁻¹ |
| T | absolute temperature | K |

Blackbody radiators are objects which are *perfect absorbers and emitters* of radiation.

Absorption of IR radiation causes **molecular vibrations** — *bending and stretching*.

4.1 Lewis Structure

Covalent bonds are formed when two neighboring atoms *share a pair of electrons*.

Only **valence electrons** — the electrons in the outermost shell — are involved; valence electrons that are *not involved* are known as **lone-pair electrons**.

Lone-pair electrons determine the shape and chemical properties of a molecule.

Stability of compounds occurs when atoms achieve **noble gas electronic configurations**, but there are exceptions to the **octet rule**:

- The **duet rule**: H₂
- The **incomplete octet**: BF₃
- The **hypervalent molecules**: SF₆, PCl₅

Drawing Lewis structures:

1. Find the total number of valence electrons.
2. Place the least electronegative atom in the center.
3. Draw a single bond from each surrounding atom to the central atom.
4. Find the remaining number of electrons.
5. Arrange the remaining electrons as lone pairs or multiple bonds to satisfy the octet rule.
6. Assign charges (if any).

4.1.1 Resonance

Resonance structures are different Lewis structures for the *same molecule* — they have the *same relative positions of atoms*, but *different bonding and lone-pair electrons*.

Resonance hybrids has a *real structure* of its *average resonance structures*. They have lower energy than any of its contributing structures.

4.1.2 Formal Charge

The extent to which an atom has *gained or lost an electron while forming covalent bonds*.

| $FC = V - L - \frac{1}{2}B$ | | |
|-----------------------------|-------------------------------|------|
| | value | unit |
| FC | formal charge | int |
| V | number of valence electrons | int |
| L | number of lone-pair electrons | int |
| B | number of bonding electrons | int |

The *sum of formal charges* equals the *actual charge* of the molecule.

The most important resonance structure:

- Minimizes formal charges.
- Minimizes separation of charges.
- Places negative formal charge on more electronegative elements.

4.2 VSEPR Model

The *valence-shell electron-pair repulsion* (VSEPR) model determines the structure around an atom by *minimizing electron-pair repulsions*.

The strength of electron-pair repulsion depends on the pair (in increasing order of strength):

- bonding pair – bonding pair
- ???
- ???

Determining molecular structure:

1. Draw the *Lewis structure*.
2. Arrange electron groups to *minimize repulsion*.
3. Identify the molecular structure from the *position of atoms*.

4.2.1 Molecular Polarity

The ??? and ??? determine *molecular polarity*, which in turn influences its physical and chemical properties.

| no. of electron groups | molecular shape | formula | no. of bonding groups | bond angle |
|------------------------|----------------------|-----------|-----------------------|---------------------------------------|
| 2 | linear | AX_2 | 2 | 180° |
| 3 | trigonal planar | AX_3 | 3 | 120° |
| | V-shaped or bent | AX_2E | 2 | $< 120^\circ$ |
| 4 | tetrahedral | AX_4 | 4 | 109.5° |
| | trigonal pyramidal | AX_3E | 3 | $< 109.5^\circ$ |
| | V-shaped or bent | AX_2E_2 | 2 | $< 109.5^\circ$ |
| 5 | trigonal bipyramidal | AX_5 | 5 | 90° (ax), 120° (eq) |
| | seesaw | AX_4E | 4 | $< 90^\circ$ (ax), $< 120^\circ$ (eq) |
| | T-shaped | AX_3E_2 | 3 | 90° (ax) |
| | linear | AX_2E_3 | 2 | 180° |
| 6 | octahedral | AX_6 | 6 | 90° |
| | square pyramidal | AX_5E | 5 | $< 90^\circ$ |
| | square planar | AX_4E_2 | 4 | 90° |