CHEM 20100 (Inorganic Chemistry I) Notes

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Topic 0

Course Prep

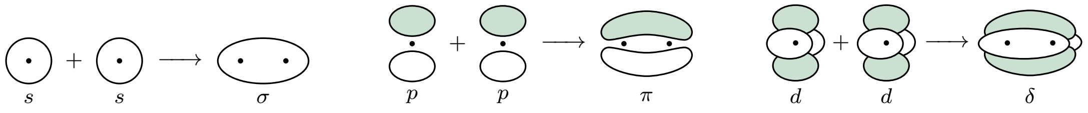
0.1 Chapter 1: Introduction to Inorganic Chemistry

From Miessler et al. (2014).

0.1.1 Notes

12/21:

- **Inorganic chemistry**: The chemistry of everything that is not organic chemistry (the chemistry of hydrocarbon compounds and their derivatives).
- **Organometallic chemistry**: The chemistry of compounds containing metal-carbon bonds and the catalysis of many organic reactions.
- There is also both **bioinorganic chemistry** and **environmental chemistry** (Miessler et al., 2014, p. 1), as well as **analytical chemistry**, **physical chemistry**, **petroleum chemistry**, **polymer chemistry** (Miessler et al., 2014, p. 4).
  - Note, though, that there are no strict dividing lines between subfields of chemistry nowadays, and most professionals work in multiple fields.
- Single, double, and triple bonds (both metal-metal and metal-carbon bonds) are found in organic and inorganic chemistry.
- Quadruple bonds exist between metal atoms in some compounds.



(a) Sigma (σ) bond. (b) Pi (π) bond. (c) Delta (δ) bond.

Figure 1: Examples of bonding interactions.

  - No such bonds exist between carbon atoms because two carbon atoms max out at a triple bond.
  - Quadruple bonds possess one sigma bond, two pi bonds, and one delta (δ) bond.
  - The delta bond is only possible with metal atoms because these atoms possess energetically accessible d orbitals.
- Quintuple bonds between transition metals have been reported, but scientists have not yet reached a consensus on to what extent these exist.

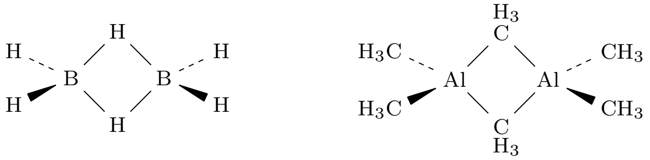


Figure 2: Inorganic compounds containing bridging hydrogens and alkyl groups.

- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 2).
- **Coordination number**: The number of other atoms, molecules, or ions to which an atom is bonded.
- "Numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher" (Miessler et al., 2014, p. 2).
  - The most common coordination geometry for transition metals is octahedral.
- 4-coordinate carbon is almost always tetrahedral. 4-coordinate metals and nonmetals can be either tetrahedral or square planar.
- **Coordination complex**: A compound with a metal as the central atom or ion and some number of **ligands** bonded to it.
- **Ligand**: An anion or neutral molecule bonded to a central atom (frequently through N, O, or S).
- **Organometallic complex**: A coordination complex where carbon (potentially bonded to other things) is one of the ligands.

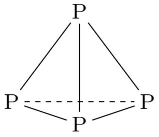


Figure 3: Tetrahedral geometry without a central atom.

- There are multiple kinds of tetrahedral structures. There is the standard arrangement seen in molecules such as methane, but there is also a form that lacks a central atom, as in elemental phosphorous P_4 (see Figure 3).
  - Other atoms such as boron and carbon also form units that surround a central cavity (e.g., icosahedral B_{12} and buckyballs C_{60}).
- Aromatic rings can bond to metals using all of their pi orbitals. This results in a metal suspended above the ring's center.
- **Cluster compound**: A compound where "a carbon atom is at the center of a polyhedron of metal atoms" (Miessler et al., 2014, p. 3).
  - There exist examples of carbon surrounded by five, six, or more metal atoms[1].
- Many new forms of elemental carbon have been discovered since the mid-1980s, notably including fullerenes (such as buckminsterfullerene, or buckyballs), carbon nanotubes, graphene, and polyyne wires.
- Miessler et al. (2014) give a brief history of inorganic chemistry for context.
  - Be aware of **crystal field theory** and **ligand field theory**.

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[1] This provides a challenge to theoretical inorganic chemists.

0.2 Chapter 2: Atomic Structure

From Miessler et al. (2014).

0.2.1 Notes

12/22:

- **Coinage metals**: Copper, silver, and gold, i.e., the transition metals in IUPAC Group 11.
- **Chalcogens**: Oxygen, sulfur, selenium, tellurium, and polonium, i.e., the nonmetals in Group 16.
- The energies of visible light emitted by the hydrogen atom are given by[2]

  $$E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$$

  where n_h is an integer greater than 2 and R_H is the Rydberg constant for hydrogen (H).
  - Note that $R_H = 1.097\times 10^7\,\text{m}^{-1} = 2.179\times 10^{-18}\,\text{J} = 13.61\,\text{eV}$.
  - This equation was first discovered by Johann Balmer in 1885.
  - Infrared and ultraviolet emissions can be described by replacing 2^2 with integers n_l^2 in the above equation on the condition that $n_l < n_h$[3].
- The energy of the light emitted is related to its wavelength, frequency, and wavenumber by the equations

  $$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

  where h is Planck's constant ($6.626\times 10^{-34}\,\text{J s}$), c is the speed of light ($2.998\times 10^8\,\text{m s}^{-1}$), and ν, λ, and $\bar{\nu}$ are the frequency, wavelength, and **wavenumber**, respectively, of the light.
- **Wavenumber**: The number of waves that exist between two points along the light's path a given distance apart. *Measured in* waves per centimeter (SI: cm^{-1}).
  - Wavenumber is proportional to energy. This is why m^{-1} or cm^{-1} can be used as an energy unit.
- **Principal quantum number**: One of the quantities n in Balmer's equation.
- Bohr's atomic theory first explained the phenomenon of Balmer's equation, positing that "electrons may absorb light of certain specific energies and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy" (Miessler et al., 2014, pp. 11–12).
  - Bohr rewrote the Rydberg constant in terms of other quantities:

    $$R = \frac{2\pi^2\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

    where...
    - ■ μ is the reduced mass of the electron/nucleus combination $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$, where $m_e = 9.11\times 10^{-31}\,\text{kg}$ is the mass of the electron and m_{nucleus} is the mass of the nucleus.
    - ■ Z is the nuclear charge.
    - ■ $e = 1.602\times 10^{-19}\,\text{C}$ is the charge of the electron.
    - ■ h is Planck's constant.
    - ■ $4\pi\varepsilon_0$ is the permittivity of a vacuum.
  - Importantly, note that the Rydberg constant for hydrogen R_H is not universal, and changes for the atom at hand based on factors like the mass of the nucleus.

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[2] Refer to Labalme (2020), specifically Figure 7.6 and the accompanying discussion.

[3] n_l denotes the lower final energy level while n_h denotes the higher initial energy level.

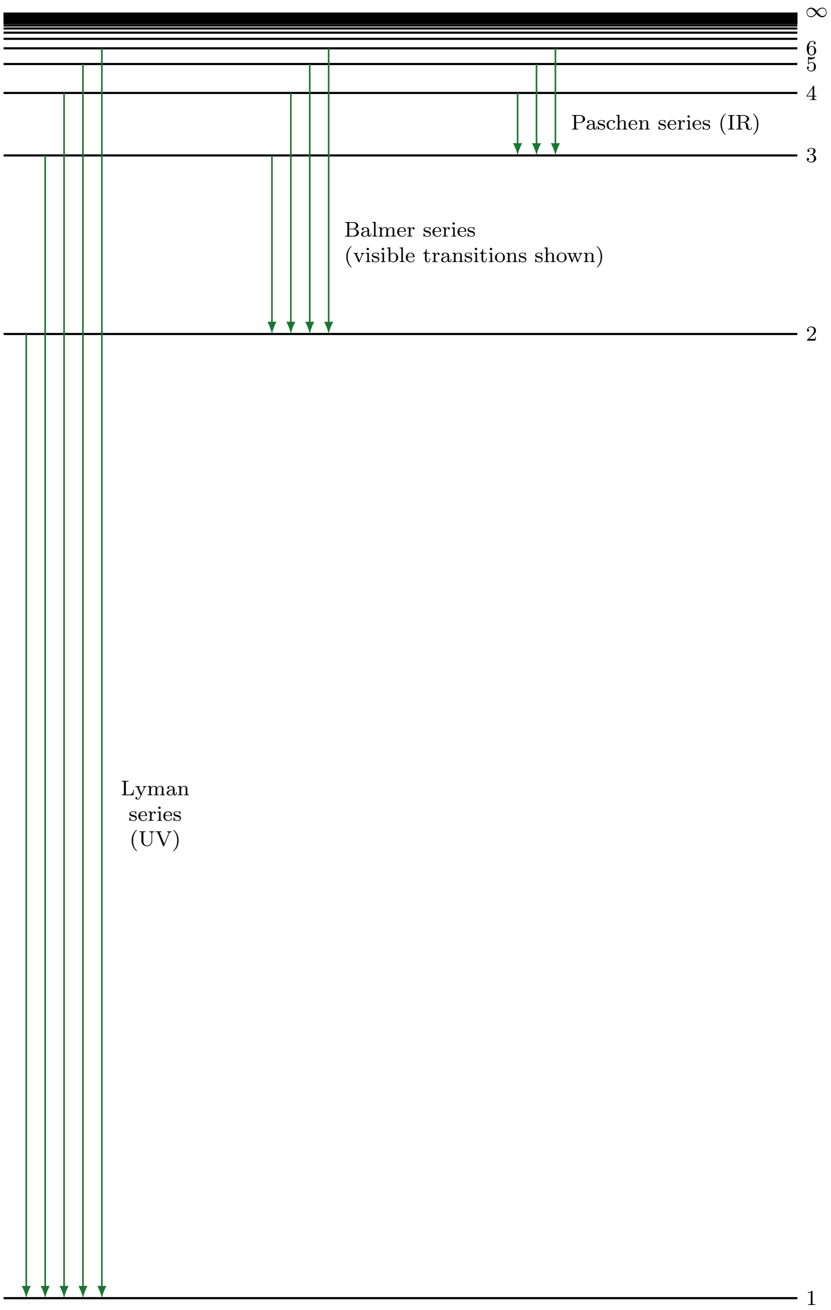
∞
6
5
4
3
2
1
Paschen series (IR)
Balmer series
(visible transitions shown)
Lyman
series
(UV)

Figure 4: Hydrogen atom energy levels.

- **Balmer series**: The four main electron transitions in hydrogen that release electromagnetic radiation in the visible spectrum.
- **Lyman series**: The five main electron transitions in hydrogen that release electromagnetic radiation in the ultraviolet spectrum.
- **Paschen series**: The three main electron transitions in hydrogen that release electromagnetic radiation in the infrared spectrum.
- "The inverse square dependence of energy on n results in energy levels that are far apart in energy at small n and become much closer in energy at larger n" (Miessler et al., 2014, p. 12)

  - Individual electrons can have more energy than they would possess in the infinite energy level, but at and above this point, the nucleus and electron are considered to be separate entities.

- **Heisenberg's uncertainty principle**: "There is a relationship between the inherent uncertainties in the location and momentum of an electron" (Miessler et al., 2014, p. 14).

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

  - The above equation describes the x-component of the uncertainty, where Δx is the uncertainty in the position of the electron and Δp_x is the uncertainty in the momentum of the electron in the x-direction.

- Because of the uncertainty principle, we cannot treat electrons as particles with precisely described motion; instead, we must describe them in **orbitals**.
- **Orbital**: A region that describes the probable locations of an electron.
- **Electron density**: "The probability of finding the electron at a particular point in space" (Miessler et al., 2014, p. 14).
  - This can be calculated in principle.
- Schrödinger and Heisenberg published (in 1926 and 1927, respectively) papers on atomic wave mechanics. Although they used very different mathematical techniques, their theories can be shown to be equivalent. However, we will introduce Schrödinger's more commonly used differential equations.
- "The Schrödinger equation describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy" (Miessler et al., 2014, p. 14).

$$H\Psi = E\Psi$$

  - In its simplest form, it is given by the above, where H is the **Hamiltonian operator**, E is the energy of the electron, and Ψ is the **wave function**.

- **Wave function**: A function that describes an electron wave in space, i.e., an atomic orbital.
- Energy values are another way of describing the quantization introduced with the Bohr model — different orbitals, characterized by different wave functions, each have characteristic energies.
- **Operator**: "An instruction or set of instructions that states what to do with the function that follows it" (Miessler et al., 2014, p. 14).
- **Hamiltonian operator**: An operator including derivatives that transforms the wave function into a constant (the energy) times Ψ. *Also known as* $\boldsymbol{\hat{H}}$.

$$H = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}$$

  - In the form used for calculating the energy levels of one-electron systems, it is given by the above, where...
    - h is Planck's constant.
    - m is the mass of the electron.
    - e is the charge of the electron.
    - $\sqrt{x^2+y^2+z^2} = r$ is the distance from the nucleus.
    - Z is the charge of the nucleus.
    - $4\pi\varepsilon_0$ is the permittivity of a vacuum.
  - The first part describes the kinetic energy of the electron, its energy of motion.

  - The second part describes the potential energy of the electron, the result of the electrostatic attraction between it and the nucleus. It is commonly designated as $V(x, y, z)$.

- "Because n varies from 1 to ∞, and every atomic orbital is described by a unique Ψ, there is no limit to the number of solutions of the Schrödinger equation for an atom. Each Ψ describes the wave properties of a given electron in a particular orbital" (Miessler et al., 2014, p. 15).
- Electron density is proportional to Ψ^2.
- Necessary conditions for a physically realistic solution for Ψ:
  1. Ψ must be single-valued: There cannot be two probabilities for an electron at any position in space.
  2. Ψ and its first derivatives must be continuous: The probability must be defined at all positions in space and cannot change abruptly from one point to the next.
  3. Ψ must approach zero as $r \to \infty$: For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).
  4. The integral
     $$\int_{\text{all space}} \Psi_A {\Psi_A}^* \, \mathrm{d}\tau = 1$$
     The total probability of an electron being somewhere in space must be 1. Applying this stipulation is called **normalizing** the wave function[4].
  5. The integral
     $$\int_{\text{all space}} \Psi_A {\Psi_B}^* \, \mathrm{d}\tau = 0$$
     Ψ_A and Ψ_B are different orbitals within the same atom, and this stipulation reflects the fact that all orbitals in the same atom must be **orthogonal** to each other.

0.2.2 Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A\sin rx + B\cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

Solution.

$$\begin{aligned}
\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2 \Psi(x)}{\partial x^2} &= E\Psi(x) \\
\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2}{\partial x^2}(A\sin rx + B\cos sx) &= E(A\sin rx + B\cos sx) \\
\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial}{\partial x}(Ar\cos rx - Bs\sin sx) &= E(A\sin rx + B\cos sx) \\
\frac{-h^2}{8\pi^2 m} \cdot \left(-Ar^2\sin rx - Bs^2\cos sx\right) &= E(A\sin rx + B\cos sx) \\
\frac{Ar^2h^2}{8\pi^2 m}\sin rx + \frac{Bs^2h^2}{8\pi^2 m}\cos sx &= AE\sin rx + BE\cos sx
\end{aligned}$$

---

[4] ${\Psi_A}^*$ denotes the complex conjugate of Ψ_A. This is necessary because wave functions may have imaginary values. However, in many cases, the wave functions are real and the integrand reduces to Ψ_A^2.

$$0 = \left(\frac{Ar^2h^2}{8\pi^2m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2m} - BE\right)\cos sx$$

Choose $x = 0$.

$$\begin{aligned} &= \frac{Bs^2h^2}{8\pi^2m} - BE \\ E &= \frac{s^2h^2}{8\pi^2m} \\ \frac{8\pi^2mE}{h^2} &= s^2 \\ s &= \sqrt{\frac{8\pi^2mE}{h^2}} \\ &\boxed{s = \sqrt{2mE}\frac{2\pi}{h}} \end{aligned}$$

With this result . . .

$$\begin{aligned} 0 &= \left(\frac{Ar^2h^2}{8\pi^2m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2m} - BE\right)\cos sx \\ &= \left(\frac{Ar^2h^2}{8\pi^2m} - AE\right)\sin rx + \left(B\left(\frac{s^2h^2}{8\pi^2m}\right) - BE\right)\cos sx \\ &= \left(\frac{Ar^2h^2}{8\pi^2m} - AE\right)\sin rx + (BE - BE)\cos sx \\ &= \left(\frac{Ar^2h^2}{8\pi^2m} - AE\right)\sin rx \end{aligned}$$

Choose $x = \frac{\pi}{2r}$.

$$\begin{aligned} &= \frac{Ar^2h^2}{8\pi^2m} - AE \\ &\boxed{r = \sqrt{2mE}\frac{2\pi}{h}} \end{aligned}$$

□

d. Show that substituting the value of r given in part c into $\Psi = A\sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned} 1 &= \int_{\text{all space}} \Psi\Psi^*\,\mathrm{d}\tau \\ &= \int_0^a \left(A\sin\frac{n\pi x}{a}\right)\left(A\sin\frac{n\pi x}{a}\right)\mathrm{d}x \\ &= \int_0^a A^2\sin^2\frac{n\pi x}{a}\,\mathrm{d}x \end{aligned}$$

Use $\sin^2 u = \frac{1-\cos 2u}{2}$.

$$
\begin{aligned}
&= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \,\mathrm{d}x \\
&= \frac{A^2}{2} \left(\int_0^a \mathrm{d}x - \int_0^a \cos \frac{2n\pi x}{a} \,\mathrm{d}x \right) \\
&= \frac{A^2}{2} \left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a \right) \\
&= \frac{A^2}{2} \left((a - 0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0 \right) \right) \\
&= \frac{A^2}{2} \left(a - \left(\frac{a}{2n\pi} \sin 2n\pi \right) \right)
\end{aligned}
$$

Since n is an integer, $\sin 2n\pi = 0$.

$$
\begin{aligned}
&= \frac{aA^2}{2} \\
\frac{2}{a} &= A^2 \\
&\boxed{A = \sqrt{\frac{2}{a}}}
\end{aligned}
$$

□

References

Labalme, S. (2020). *AP chemistry notes* (Accessed 22 December 2020.). https://github.com/shadypuck/APChemNotes/blob/master/main.pdf

Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic chemistry* (fifth). Pearson Education.