

Please Note: This sheet is intended to assist students in reviewing for the midterm exam. It is not intended to be comprehensive (i.e. there may be errors or omissions).

Absorption and emission Spectra of Atomic Hydrogen

1. $E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$
2. Rydberg equations
 - a) $\Delta E = R_H Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$, $R_H = 13.6 \text{ eV} = 2.18 \times 10^{18} \text{ J}$
 - b) $\Delta\nu = \frac{R_H Z^2}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ Hz}$ and $\Delta\bar{\nu} = \frac{\Delta E}{hc}$ (preferred units cm^{-1})
 - c) For emission: Lyman $n_f = 1$; Balmer $n_f = 2$; Paschen $n_f = 3$

Bohr Theory

1. Works only for 1 electron atoms and ions.
2. Bohr used the classical equations for a negatively charged particle revolving around a heavier positive particle; i.e. that the electrostatic force on the electron equals the centripetal force on the electron in an orbital:

$$F_{ele} = \frac{Ze^2}{4\pi\epsilon_0 r^2}; \text{ and } F_{cent} = \frac{m_e v^2}{r}$$

where m_e is the mass of the electron, v the velocity of the electron and r the radius of the orbit.

3. Bohr postulated that only specific values of the angular momentum are allowed:

$$m_e v r = n\hbar = n \frac{h}{2\pi}, \text{ where } n \text{ is an integer}$$

$$\text{This gives } r_n = \frac{n^2}{Z} a_0 \text{ and } a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e e^2}$$

4. The orbital energy is given by the classical equations:

$$E = KE + PE = \frac{1}{2} m v^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Z^2}{n^2} R_H$$

Quantum Mechanics

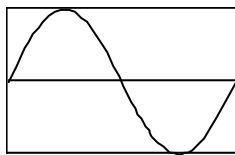
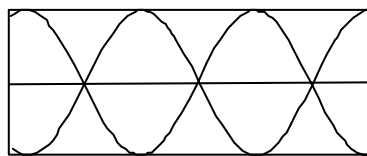
1. DeBroglie Wave: $\lambda = \frac{h}{mv} = \frac{h}{p}$

2. Heisenberg Uncertainty Principle:

$$\Delta p \Delta x \geq \frac{\hbar}{2}; \text{ or } \Delta E \Delta t \geq \frac{\hbar}{2}$$

$$p = mv \Rightarrow \Delta p = m \Delta v \text{ and } \lambda = \frac{h}{p} \Rightarrow \Delta \lambda = -\frac{h}{p^2} \Delta p$$

3. 1D Wave

Standing wave
with one nodeNot a standing wave
ends not tied down not allowed

Boundary conditions: Ends tied down standing wave
More nodes \rightarrow higher energy

4. 2D waves for a square or round drum have degenerate sets (i.e. two or more waves have the same energy. They are the same wave only rotated in space.

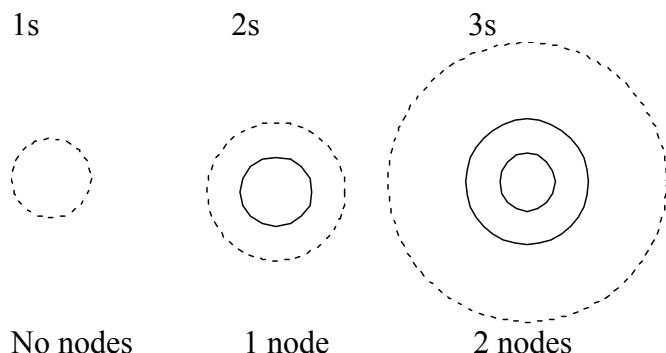
Schrödinger Equations: 3D wavefunctions $\Psi(r)$ or Orbitals

- Boundary conditions: $\Psi(r) \Rightarrow 0$ as $r \Rightarrow \pm\infty$ (this is same as standing wave and makes probability finite) and $\Psi(r) < \infty$; at all times
- $\Psi(r)^2 dV$ is probability of finding an electron in small volume dV around r
- Only solutions with specific values of the quantum numbers, n, l, m_l (and m_s added later) are allowed.
- $\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_{lm_l}(\theta, \phi)$
- $\int_{-\infty}^{\infty} \Psi(r)^2 dV = \int_{-\infty}^{\infty} R_{nl}(r)Y_{lm_l}(\theta, \phi)r^2 \sin(\theta)drd\theta d\phi = 1$
- Probability of finding a particle at a distance r from the nucleus for any angles θ and ϕ is given as $P(r) = r^2 [R_{nl}(r)]^2$

Quantum Numbers

- $n \rightarrow$ principle = total number of nodes + 1, mostly determines the energy and orbital size
- $l \rightarrow$ orbital shape quantum number = number of angular nodes has some effect on energy and size in multielectron atoms
- $m_l \rightarrow$ orientation quantum number (degeneracy of the l orbital is $2l + 1$) values $-l, -l + 1, \dots, 0, 1, 2, \dots, l$ determines the orientation of the orbital in space
- m_s spin quantum number $+\frac{1}{2}$ and $-\frac{1}{2}$

Orbit type	l	m_l	degeneracy	# of electrons in orbital
<i>s</i>	0	0	1	2
<i>p</i>	1	-1, 0, 1	3	6
<i>d</i>	2	-2, -1, 0, 1, 2	5	10
<i>f</i>	3	-3, -2, -1, 0, 1, 2, 3	7	14

Orbitals Sizes, Shapes, and graphs

Look at pictures of the hydrogen orbitals at <http://www.shef.ac.uk/chemistry/orbitron/>. Note particularly the shape, nodes and sign of the orbitals. Note that the s and d orbitals are symmetric to inversion through the origin while the p is anti-symmetric toward inversions.

Orbital energy

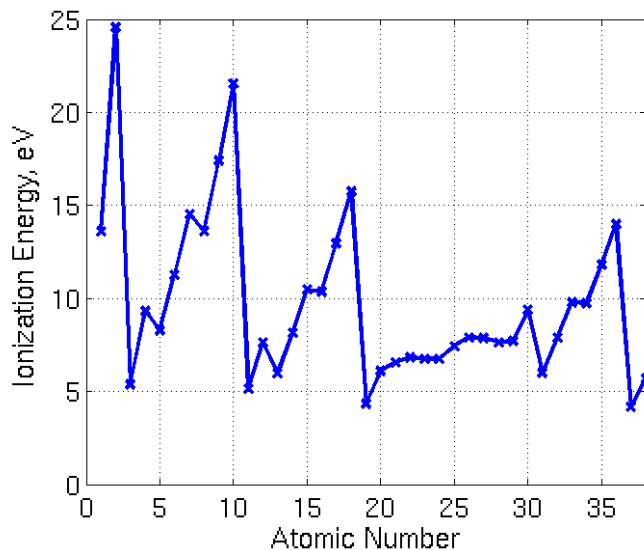
- For one-electron atoms the energy depends only on n
- For multi-electron atoms:
 - Penetration for orbitals of same n gives energy order of $ns < np < nd < nf < \dots$
 - General orbital energy order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 5p
- Exceptions: Neutral atoms: Cr, Cu, Nb, and Mo.
Ions: all transition metals when they ionize the first two electrons that are lost are from the ns shell not the (n-1)d shell.

Filling orbitals

1. Pauli Principle: Every electron must have a unique set of 4 quantum numbers
2. Aufbau principle: Fill lowest energy orbitals first
3. Hund's Rule: In a degenerate orbital aligned spins have lower energy than paired spins

Periodic Trends

- Atomic size increases as you move down the periodic table (PT) and decreases as you move across to the right.
- When you add 1 electron (to a partially filled orbital) and 1 proton, the added electrons do not completely shield the added positive charge. Thus the effective nuclear charge goes up and the electrons are held more tightly, ionization energy goes up, and the atom becomes smaller.
- When you add an electron to a completely empty orbital of a larger n the size of the atom will get much larger and the ionization energy will go down.
- Ionization Energy decreases as you move down the periodic table and increases as you move to the right.



Exceptions to general trends

- Closed shells, closed sub-shells ($2p^6$, $3p^6$, $3d^{10}$) and half-filled sub-shells ($2p^3$, $3p^3$, $3d^5$) are stable and have higher ionization energies.
- p electrons are better shielded compared to s (p electrons do **not** penetrate as close to the nucleus as do the s). Thus the atom with $[\text{He}]2s^2 2p^1$ is easier to ionize than one with $[\text{He}]2s^2$
- When you have one more electron than a half filled subshell the electrons must pair and thus two electrons share the same sub-orbital. Due to electron-electron repulsion this electron is easier to ionize.

Lewis structures

Rules:

1. Total number of valence electrons is sum of valence electrons of each atom minus the overall charge.
2. Arrange the atoms in a structure and distribute the electrons so that each atom has 8 electrons around it (exceptions, H has 2, B can have 6 and third row and lower atoms can have more than 8).
3. Try to maximize the number of bonds that each atom has.
4. Calculate the partial charge on each atom (it must add up to the total charge).
5. See if you can optimize the structure to reduce partial charges. Put negative partial charges on electronegative atoms and positive on electropositive atoms and maximize the bonds to all atoms.
6. Look for resonance structures.

Resonance Structures

1. To form resonance structures you can move electrons but not atoms.
2. Structures with higher partial charges are less stable.
3. Structures with negative charges on electropositive atoms are not favorable.
4. Structures with positive charges on electronegative atoms are not favorable

Oxoacids

The four rules of Oxoacids are:

1. As electronegativity of central atom increases the acidity increases.
2. As the positive formal charge (no expanded octet) on the central atom increases the acidity increases.
3. As the number of resonance structures of the dissociated acid increase the acidity increases.
4. As the number of O atoms that do not have an attached H increases acidity increases.