General Chemistry I
Tutorial 05

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Outline

Quiz 5.1

A Li atom has two electrons in its 1s orbital and one electron in its 2s orbital. The effective nuclear charge for the 2s orbital is $Z_{eff}(2s) = 1.28$. Given Ry $= 13.6$ eV, estimate the energy (in eV) of the 2s orbital of Li.

Quiz 5.2

What are the two aspects of Aufbau Principle?

PS 3.1

Using Table 5.2, write down the mathematical expression for the $2p_x$ wave function for an electronically excited H atom. Estimate the probability of finding the $2p_x$ electron if you look in a cubical box of volume of $0.8pm^3$ centered at a distance of5.0×10^{-10} m in the $\theta = \pi/2$, $\psi = 0$ direction. Does this probability change as you change ψ? At what ψ angles is the probability of finding the electron smallest and at what ψ angles is the probability the largest? (Note that $\psi = 2\pi$ is the same location as $\psi = 0$, so don't double count.)

	Angular Part $Y(\theta, \phi)$	Radial Part $R_{n\ell}(r)$
$\ell = 0$	$Y_s = \left(\frac{1}{4\pi}\right)^{1/2}$	$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-\sigma)$
		$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)\exp(-\sigma/2)$
		$R_{3s} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)\exp(-\sigma/3)$
$\ell = 1$	$Y_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$	$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma\exp(-\sigma/2)$
	$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)\exp(-\sigma/3)$
	$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$\ell = 2$	$Y_{d_{z^2}} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2\exp(-\sigma/3)$
	$Y_{d_{xz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$	
	$Y_{d_{yz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$	
	$Y_{d_{xy}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$	
	$Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$	

PS 3.2

Use the mathematical expression for the 2p zwave function of a one-electron atom (see Table 5.2) to show that the probability of finding an electron in that orbital anywhere in the x-y plane is 0. What are the nodal planes for a d_{xz} orbital and for a $d_{x^2-y^2}$ orbital?

PS 3.3

The wave function of an electron in the lowest (that is, ground) state of the hydrogen atom is:

$$\psi(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp\left(-\frac{r}{a_0}\right)$$

(a) What is the probability of finding the electron inside a sphere of volume 1.0pm^3, centered at the nucleus?
(b) What is the probability of finding the electron in a volume of 1.0 pm^{3}at a distance of 52.9 pm from the nucleus, in a fixed but arbitrary direction?
(c) What is the probability of finding the electron in a spherical shell of 1.0 pm in thickness, at a distance of 52.9 pm from the nucleus?

PS 3.4

The nitrogen atom has one electron in each of the $2p_x$, $2p_y$, and $2p_z$ orbitals. By using the form of the angular wave functions, show that the total electron density, $\psi^2(2p_x) + \psi^2(2p_y) + \psi^2(2p_z)$ is spherically symmetric (that is, independent of angle θ and ϕ).

PS 3.5

The outermost electron in an alkali-metal atom is sometimes described as resembling an electron in the corresponding state of a one-electron atom. Look up the first ionization energy of lithium, compare it with the binding energy of a 2s electron in a oneelectron atom that has nuclear charge Z_{eff} , and determine the value of Z_{eff} that is necessary for the two energies to agree. Repeat the calculation for the 3s electron of sodium and the 4s electron of potassium.

Slater rules

Firstly, the electrons are arranged into a sequence of groups in order of increasing principle quantum number n, and for equal n in order of increasing angular quantum number l, expect that s- and p- orbitals are kept together.

$$[1s][2s,2p][3s,3p][3d][4s,4p][4d][4f][5s,5p][5d] \text{ etc.}$$

The shielding constant(σ) for each group is formed as the sum of following contributions:

- Outer electrons have no shielding effect on inner electrons.
- For electrons within the same group: $\sigma = 0.35$(for 1s: $\sigma = 0.31$)
- For s,p electrons, shielding constant originated from adjacent group is 0.85, for d,f electrons adjacent group contribute 1.00 to σ.
- More inner electrons give rise to shielding constant of 1.

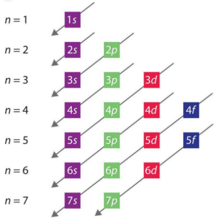
Using slater rules, please calculate effective charge of 2p electrons of carbon atom.

$$Z_{eff} = Z - \sigma = 6 - (0.35 \times 3 + 0.85 \times 2) = 3.25$$

Configuration of Electrons

The **ground-state** electronic configuration is built up by Hartree atomic orbitals in order of increasing energy and adding one electron at a time, starting with the lowest energy orbital.

For 4s or 3d, which is of lower energy?
For K and Ca,calculations show that $\varepsilon_{4s} < \varepsilon_{3d}$.
For Sc and element beyond, calculations show that $\varepsilon_{3d} < \varepsilon_{4s}$.
But electrons in 3d orbitals experience
greater electronic repulsion, electronic confuguration of
Sc is [Ar]$4s^2 3d^1$, the same is true for other d-block element.



K: [Ar]$4s^1$, Ca: [Ar]$4s^2$
V: [Ar] $4s^2 3d^3$, Cr:[Ar] $4s^1 3d^5$
Ni: [Ar] $4s^2 3d^8$, Cu: [Ar] $4s^1 3d^{10}$

Outermost electron is always the one to be ionized first. The order of ionization do not always follow the order of electron filling.