Homework 4

(0.6')1. Photoelectron spectroscopy studies have determined the orbital energies for fluorine atoms to be

1*s*	-689 eV
2*s*	-34 eV
2*p*	-12 eV

Estimate the value of Z_{eff} for F in each of these orbitals.

$E=-Z_{eff}^2/n^2$

$Z_{1s}=7.12$ $Z_{2s}=3.2$ $Z_{2p}=1.9$

(0.6')2. Without consulting any tables, arrange the following substances in order and explain your choice of order:

(a) Mg^{2+}, Ar, Br^-, Ca^{2+} in order of increasing radius

(b) Na, Na^+, O, Ne in order of increasing ionization energy

(c) H, F, Al, O in order of increasing electronegativity

(a) $Mg^{2+} < Ca^{2+} < Ar < Br^-$

(b) $Na < O < Ne < Na^+$

(c) $Al < H < O < F$

(0.6')3. Suppose an atom in an excited state can return to the ground state in two steps. It frst falls to an intermediate state, emitting radiation of wavelength λ_1, and then to the ground state, emitting radiation of wavelength λ_2. The same atom can also return to the ground state in one step, with the emission of radiation of wavelength λ. How are λ_1, λ_2, and λ related? How are the frequencies of the three radiations related?

$\Delta E_{总}=\Delta E_1+\Delta E_2$ $\therefore 1/\lambda_{总}=1/\lambda_1+1/\lambda_2$ $\nu_{总}=\nu_1+\nu_2$

(0.8')4. The wave function of an electron in the lowest (that is, ground) state of the hydrogen a

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

$$a_0=0.529\times10^{-10}\ \text{m}$$

(a) What is the probability of finding the electron inside a sphere of volume 1.0 pm^3, centered at the nucleus (1 pm = 10^{-12} m)?

(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?

a) The small sphere centered at the nucleus of the H atom has a volume of 1 pm^3 (1.0×10^{-36} m^3). Over the very short distance between the center and surface of this sphere, ψ^2 stays nearly constant at 2.15×10^{30} m^{-3}, and

$$\text{probability} = (2.15 \times 10^{30}\ \mathrm{m}^{-3}) \times (1.00 \times 10^{-36}\ \mathrm{m}^3) = 2.15 \times 10^{-6}$$

b) At $r = 52.9$ pm ($r = a_0$), ψ_{1s}^2 evaluates to *less* than at $r = 0$:

$$\psi_{1s}^2\,(r = a_0) = (2.15 \times 10^{30}\ \mathrm{m}^{-3})\mathrm{e}^{-2} = 2.91 \times 10^{29}\ \mathrm{m}^{-3}$$

Assume that ψ_{1s}^2 is constant throughout the 1 pm^3 volume that the problem specifies. The chance of finding the electron at 52.9 pm in a fixed direction is

$$\text{probability} = (2.91 \times 10^{29}\ \mathrm{m}^{-3})(1.0 \times 10^{-36}\,\mathrm{m}^3) = 2.91 \times 10^{-7}$$

c) A spherical shell of thickness 1 pm and radius 52.9 pm has a volume

$$V_{\text{shell}} = 4\pi r^2 \Delta r = 4\pi (52.9\ \mathrm{pm})^2\ (1\ \mathrm{pm}) = 3.52 \times 10^{-32}\ \mathrm{m}^3$$

This larger volume (35200 pm^3) is more likely to contain the electron than the tiny 1 pm^3 volume element considered in part **b)**

$$\text{probability} = (2.91 \times 10^{29}\ \mathrm{m}^{-3})(3.52 \times 10^{-32}\ \mathrm{m}^3) = 0.0102$$

(0.6')5. (a) 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, it is independent of the angles θ and ϕ). The neon atom, which has two electrons in each 2p orbital, is also spherically symmetric.

(b) The same result as in part (a) applies to d orbitals, thus a filled or half-filled subshell of d orbitals is spherically symmetric. Identify the spherically symmetric atoms or ions among the following: F^-, Na, Si, S^{2-}, Ar^+, Ni, Cu, Mo, Rh, Sb, W, Au.

a)

$$Y(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\varphi \qquad Y(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\varphi \qquad Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

The radial parts of the wave functions need not be taken into account because they do not affect the angular symmetry.

$$\begin{aligned} Y^2(p_x) + Y^2(p_y) + Y^2(p_z) &= \left(\frac{3}{4\pi}\right)(\sin^2\theta\cos^2\varphi + \sin^2\theta\sin^2\varphi + \cos^2\theta) \\ &= \left(\frac{3}{4\pi}\right)(\sin^2\theta(\cos^2\varphi + \sin^2\varphi) + \cos^2\theta) \\ &= \left(\frac{3}{4\pi}\right)(\sin^2\theta(1) + \cos^2\theta) = \frac{3}{4\pi} \end{aligned}$$

The N atom is spherically symmetric because ψ^2 is independent of θ and φ.

b) The following species are spherically symmetric: F^-, Na, S^{2-}, Cu, Mo, Sb, Au.

(0.8')6. (a) Give the complete electron configuration ($1s^2 2s^2 2p$ ...) of aluminum in the ground state.

(b) The wavelength of the radiation emitted when the outermost electron of aluminum falls from the 4s state to the ground state is about 395 nm. Calculate the energy separation (in joules) between these two states in the Al atom.

(c) When the outermost electron in aluminum falls from the 3d state to the ground state, the radiation emitted has a wavelength of about 310 nm. Draw an energy-level diagram of the states and transitions discussed here and in (b). Calculate the separation (in joules) between the 3d and 4s states in aluminum. Indicate clearly which has higher energy.

a) Ground-state Al: $1s^2 2s^2 2p^6 3s^2 3p^1$.

b)

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{J s})(2.998 \times 10^{8} \text{ m s}^{-1})}{395 \times 10^{-9} \text{ m}} = 5.03 \times 10^{-19} \text{ J}$$

c) The energy level diagram for Al