QMS Problem set 5 (due 18.2.2021)

Warm-up: (Each warm-up is connected to one of the problems (first warm-up to first problem etc.))

W1: Answer problem E8A.7(a) (1 points)

E8A.7(a) The wavefunction of one of the d orbitals is proportional to $\cos\theta \sin\theta \cos\phi$. At what angles does it have nodal planes?

W2: Answer problem E8C.1(a) (1 points)

E8C.1(a) Identify the transition responsible for the shortest and longest wavelength lines in the Lyman series.

W3: Answer problem P9B.2 (4 points)

P9B.2 Imagine a small electron-sensitive probe of volume 1.00 pm^3 inserted into an H_2^+ molecule-ion in its ground state. Calculate the probability that it will register the presence of an electron at the following positions: (a) at nucleus A, (b) at nucleus B, (c) half way between A and B, (d) at a point 20 pm along the bond from A and 10 pm perpendicularly. Do the same for the molecule-ion the instant after the electron has been excited into the antibonding LCAO-MO. Take $R = 2.00a_0$.

Hint: The volume of the probe is so small that the wavefunction can be assumed to stay constant inside the probe.

W4: Fill in the final conceptual questionnaire for the course. (3 points)

Problems:

P1: Answer P8A.5 parts b), c) and d) (6 points)

For this exercise form the wavefunction of 3s orbital using Atkins' tables as instructed. Please find the wavefunctions for $3p_x$ and $3d_{xy}$ provided below.

For the calculations and plotting it is strongly recommended to use a numerical program like Desmos, Mathematica, Python, etc...

P8A.5 Explicit expressions for hydrogenic orbitals are given in Tables 7F.1 (for the angular component) and 8A.1 (for the radial component). (a) Verify both that the $3p_x$ orbital is normalized (to 1) and that $3p_x$ and $3d_{xy}$ are mutually orthogonal. *Hint:* It is sufficient to show that the functions eiϕ and e2iϕ are mutually orthogonal. (b) Identify the positions of both the radial nodes and nodal planes of the 3s, $3p_x$, and $3d_{xy}$ orbitals. (c) Calculate the mean radius of the 3s orbital. *Hint:* Use mathematical software. (d) Draw a graph of the radial distribution function for the three orbitals (of part (b)) and discuss the significance of the graphs for interpreting the properties of many-electron atoms.

$$\psi_{3p_x}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right)e^{-r/3a_0}\sin\theta\cos\phi$$

$$\psi_{3d_{xy}}(r,\theta,\phi) = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\sin 2\phi$$

P2: Answer P8C.4 (4 points)

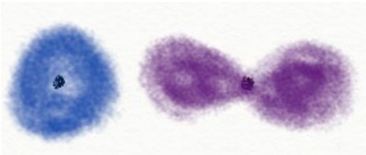
P8C.4 The Li^{2+} ion is hydrogenic and has a Lyman series at 740 747 cm^{-1}, 877 924 cm^{-1}, 925 933 cm^{-1}, and beyond. Show that the energy levels are of the form $-hc\tilde{R}_{Li}/n^2$ and find the value of $\tilde{R}_{Li}$ for this ion. Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and find its ionization energy.

Hint: why not use a computer here as well?

P3: Answer P9C.2 (5 points)

P9C.2 Before doing a calculation, sketch how the overlap between a 1s orbital and a 2p orbital directed towards it can be expected to depend on their separation. The overlap integral between an H1s orbital and an H2p orbital directed towards it on nuclei separated by a distance R is S $S=(R/a_0)\{1+(R/a_0)+\frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$. Plot this function, and find the separation for which the overlap is a maximum.

Hint: in your sketch the s- and p-orbitals can look for example like this:



For the plotting of the function it is recommended to use a computer again :)