

Structure of Matter - midterm 1

Problem 1

7g electron in atomic hydrogen

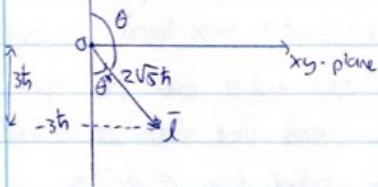
a) g-electron $\rightarrow l=4$
 $m = -3$

letter	s	p	d	f	g
l	0	1	2	3	4

$$|\vec{l}| = \sqrt{l(l+1)} \hbar = 2\sqrt{5} \hbar$$

$$l_z = m \hbar = -3 \hbar$$

\vec{z} polar angle θ is the angle \vec{l} makes with the positive z-axis



$$\theta^* = \cos^{-1}\left(\frac{3\hbar}{2\sqrt{5}\hbar}\right) = 47.9^\circ$$

$$\theta = 180^\circ - \theta^* = 132.1^\circ$$

The requested polar angle is 132.1°

OR, direct method:

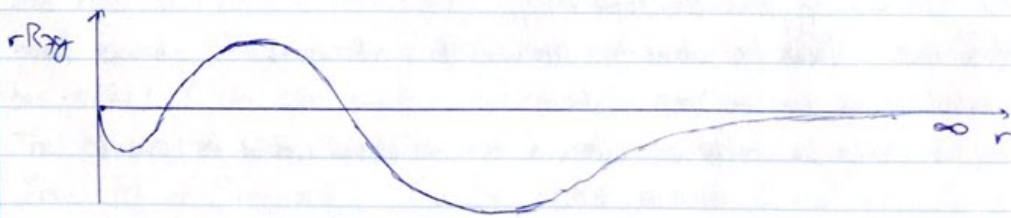
$$\theta = \cos^{-1}\left(\frac{-3\hbar}{2\sqrt{5}\hbar}\right) = 132.1^\circ$$

b) 7g $\rightarrow n=7$

$$\# \text{ nodes} = n - l - 1 = 7 - 4 - 1 = 2$$

By convention, the first lobe is negative
successive lobes become longer.

The last lobe exponentially decays to zero



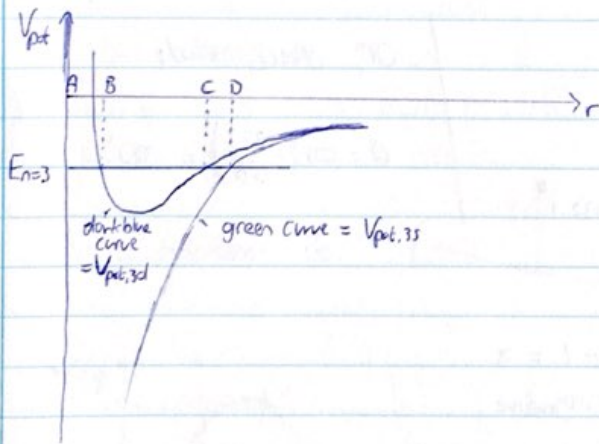
c) $3s : l=0$
 $3d : l=2$

For the 3s wavefunction, the centrifugal potential ^{energy} is zero because $l=0$. Therefore, the potential energy is given by the Coulomb potential energy only.

For the 3d wavefunction, the centrifugal potential is not zero but given by $V_{\text{cent}} = \frac{\hbar^2 l(l+1)}{2mr^2}$ and depicted by the yellow curve. The potential energy is then given by the sum of this centrifugal potential energy and the Coulomb potential energy (green curve), and is represented by the dash-blue curve.

The energy of the 3s and 3d wavefunction is ~~the same~~ the same and is indicated by the dashed $E_{n=3}$ line.

In principle, ~~the wavefunction~~ the wavefunction can extend over the region where the eigen energy of the state ~~is higher~~ is higher than the potential energy. This means that the 3s wavefunction can extend from A to D,



and the 3d wavefunction from B to C.
 \Rightarrow 3s wavefunction is more extended than the 3d wavefunction.

d) 2s. There is also 2p, but not 2d or higher ($l=0, \dots, n-1$)

And 2s and 2p have the same energy.

The $n=2$ level ~~should~~ ^{should} lie above b, otherwise it is not enough to overcome the potential energy for the 2p electron.

Also, it should lie below c, otherwise a d electron would be possible.

energy range of 2s: between b and c

20 Fe^{7+} Ion. pot. is 151 eV
 $1s^2 2s^2 2p^6 3s^2 3p^4 3d$
 Z protons, $Z-7$ electrons

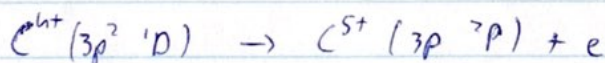
$$a) E_{\text{ion}} = +13.6 \frac{Z_{\text{eff}}^2}{n^2} \text{ [eV]} \quad \rightarrow \quad Z_{\text{eff}} = \sqrt{\frac{E_{\text{ion}}}{13.6}} n$$

The binding energy of the 3d electron is 151 eV ; $n=3$

$$Z_{\text{eff}} = \sqrt{\frac{151}{13.6}} \cdot 3 \approx 10$$

b) There are $Z-8$ electrons 'between' the nucleus and the 3d electron. They shield the nucleus. So you could expect the 3d to see eff Z of $8+$. But they are not always in between. ~~So~~ There is also a small probability for the 3d electron to be at some small value of r , where there are fewer electrons to shield the nucleus. Therefore the effective charge is higher than $8+$.

c) C^{4+} $3p^2$ 1D ($L=2, S=0$) $E_{\text{ion}} = +100 \text{ eV}$ (of term)



hydrogen-like system!

$$E_{\text{ion}} = -13.6 \frac{Z^2}{n^2}$$

$$Z_{\text{carbon}} = 6$$

$$\left. \begin{array}{l} E_{\text{ion}} = -13.6 \frac{Z^2}{n^2} \\ Z_{\text{carbon}} = 6 \end{array} \right\} E_{3p} = -13.6 \frac{6^2}{3^2} = -13.6 \cdot 4 = -54.4 \text{ eV}$$

The energy changes from -100 eV to -54.4 eV, so the ionization energy of the $3p^2 \ ^1D$ term is 45.6 eV ($-54.4 - (-100 \text{ eV})$)

zd) IPM: each electron experiences an average potential of the nucleus and all other electrons. This enables us to write $H = h_1 + h_2 + \dots$ and thus also $E = E_1 + E_2 + \dots$

In our case now, the electrons are equivalent. Each 3p electron experiences the same average potential of the $6+$ nucleus and 1 3p electron. Therefore, their contribution to the total energy is the same and they see the same effective charge.

So we consider one 3p electron with binding energy $\frac{100}{2} \text{ eV} = 50 \text{ eV}$

$$Z_{\text{eff}} = \sqrt{\frac{E_{\text{bin}}}{13.6}} n = \sqrt{\frac{50}{13.6}} \cdot 3 = 5.75$$

Each of the two electrons experiences an effective nuclear charge of 5.75 +

Problem 3

a) Zr: $[Kr] 5s^2 4d^2$

filled subshells: $L=0, S=0$

So we only have to consider $4d^2$

$$l_1 = 2, l_2 = 2$$

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$$

$$L = |l_1 - l_2|, |l_1 - l_2 + 1|, \dots, l_1 + l_2 = 0, 1, 2, 3, 4$$

$$S = |s_1 - s_2|, |s_1 - s_2 + 1|, \dots, s_1 + s_2 = 0, 1$$

Because the 2 $4d$ electrons are equivalent, we have to make sure not to violate the Pauli exclusion principle by satisfying the following rule: $L+S$ is even

For the singlet terms ($S=0$), this means that $L=1$ and $L=3$ are not allowed.

For the triplet terms ($S=1$), this means that $L=0, L=2$, and $L=4$ are not allowed.

Term notation: $2S+1 L$

Allowed terms: $^1S, ^1D, ^1G, ^3P, ^3F$

b) Tb: $[Xe] 6s^2 4f^9$
 $L=0, S=0$

We only have to consider $4f^9$

The f subshell ($l=3$) can accommodate $2(2 \cdot 3 + 1) = 14$ electrons.

Considering 9 $4f$ electrons is equivalent to considering $14 - 9 = 5$ holes (also $l_i = 3, s_i = \frac{1}{2}$)

So, we consider $4f^5$

To determine the ground term and level we use Hund's rules.

First, we have to maximise S . The max S you can get from 5 $s = \frac{1}{2}$ particles is $S = \frac{5}{2}$.

This means that $M_S = \frac{5}{2}$ must exist. This can only be achieved if the 5 holes each have $m_s = \frac{1}{2}$. Then, to not violate the Pauli exclusion principle, their m_l values must all be different (The other quantum numbers n, l, s , and now also m_s , are already the same)

The combination with the highest sum is $m_{l1} = 3, m_{l2} = 2, m_{l3} = 1, m_{l4} = 0, m_{l5} = -1$.

Then, $M_L = \sum m_{li} = 5$. So the highest possible L is $L=5$.

Now we can write down the ground term: 6H

For the ground level, we have to look at the occupancy of the original subshell.

It is more than half filled, as there are 9 out of 14 filled.

According to Hund's rules then, the highest possible J then corresponds to the ground level.

$$J_{\max} = L + S = 5 + \frac{5}{2} = \frac{15}{2}$$

So the ground level is ${}^6H_{15/2}$