Exam 09-03-2026

Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

1) a)

$Z = 20$

$$H = \sum_{i=1}^{20} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j}^{20} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right] =$$

$$= \underbrace{\sum_{i=1}^{20} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2}_{K} \underbrace{- \frac{20 \cdot e^2}{4\pi\varepsilon_0 r_i} \right]}_{V_{N-e}} + \underbrace{\sum_{i \neq j}^{20} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{V_{ee}}$$

b). K - kinetic energy of the 20 electrons

V_{N-e} - attraction between each of the electrons and the nucleus

V_{ee} - repulsion berbween all pairs of electrons.

c). Central Field approximation:

We replace the explicit repulsion between electrons by a potential that depends on coordinates of a single electron $\frac{1}{r_{ij}} \rightarrow u(r_i)$. This is the <u>independent particle</u> model. Then, we can express the many-electron WF as an ~~[illegible]~~ (antisymmetrized product of 1-e^- orbitals.

For atoms, we can also assume that $u(r_i)$ is spherically symmetric. We then replace the attraction to the nucleus and $u(r_i)$ by the central field potential:

$$V_{CF}(r_i) = -\frac{Ze^2}{4\pi\varepsilon_0 r_i} + S(r_i)$$

$$H_{CF} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{CF}(r_i) \right\}$$

d). We do not know what $V_{CF}(r_i)$ or $U(r_i)$ is. Naivelly, we can say that $U(r_i)$ represents the repulsion between the electron i and the electron density due to the rest of the electrons. However, to know the density we need to know the wavefunctions. This is a self-consistent problem and we will solve it iterativelly (use an initial guess for $U(r_i)$,

$\longleftrightarrow$

Ca^+ $[\ ]4s$ $IP = 11{,}872$ eV

e) $[\ ]4d$ $IP = 4{,}824$ eV

$$\varepsilon_{n,l} = \frac{-13.6\,\text{eV}\,(q'+1)^2}{(n-\delta_l)^2} \qquad q' = 1 \quad (Ca^+ \text{ ion}) \qquad n = 4$$

4s: $$-11{,}872 = \frac{-13{,}6 \cdot 4}{(4-\delta_l)^2}$$

$$(4-\delta_{4s})^2 = 4{,}58 \qquad 4 - \delta_{4s} = 2{,}14$$

$$\delta = 1{,}86$$

4d: $$(4-\delta_{4d})^2 = 11{,}276 \qquad \delta_{4d} = 4 - 3{,}36 = 0{,}63$$

f). This is because 4s penetrates more into the core than 4d → the electron sees higher effective

2) a).

$n=3 \qquad \epsilon = 1407090 6{,}59\ cm^{-1}$

$$\epsilon_n = -\frac{R_N}{n^2} \qquad R_N = Z^2 R_\infty$$

$$\Delta\epsilon = \left(-\frac{R_N}{3^2} - \left(-\frac{R_N}{1^2}\right)\right) = -\frac{R_N}{9} + R_N = \frac{8}{9}R_N =$$

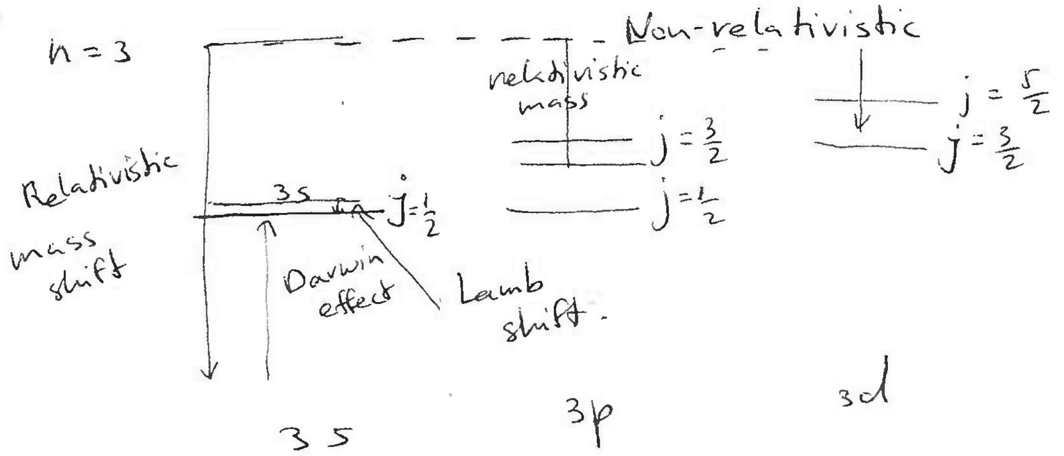
$$1\,407\,090\,6{,}59\ cm^{-1}$$

$\frac{8}{9}R_N = 1744\ eV \qquad R_N = 1962\ eV \Rightarrow Z^2 \cdot 13{,}6 = 1962\ eV$

$Z^2 = 144\ , \quad Z = 12$

This is Mg.

(b).



$Z=12$

b). 3d $\quad j_1 = \frac{3}{2}$
$\quad j_2 = \frac{5}{2}$.

$$\beta_{3d} = \frac{\alpha^2 Z^2}{n\ell(\ell+1)}\epsilon(n) = \frac{\alpha^2 Z^2}{3\cdot 2\cdot 3}\frac{1962\ eV}{9} =$$

$$= 0{,}093\ eV$$

$$\Delta\epsilon = j_2 \cdot \beta_{3d} = \frac{5}{2}\cdot\beta_{3d} = 0{,}23\ eV$$

d) $\tilde{\nu} = R_\mu \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

Lyman α $\quad n_1 = 1$

$n_2 = 2.$

$$R_\mu = R_\infty \left[1 - \frac{m_\mu}{m_p} \right] = R_\infty \left[1 - 207 \cdot \underbrace{\frac{m_e}{m_p}}_{1836} \right] = \underset{eV}{12.066} =$$

$$= 97329 \text{ cm}^{-1}$$

$$\tilde{\nu}_{L\alpha} = 97329 \left[1 - \frac{1}{4} \right] = 72997.3 \text{ cm}^{-1}$$

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4). Sr : $[\quad] 5s^2$

a). ${}^1S_0$, even parity $-1^{0+0} = 1.$

b). $5s4d$ $\quad l_1 = 0, \; s_1 = \frac{1}{2}$

$l_2 = 2, \; s_2 = \frac{1}{2}$

$L = 2$

$S = 0, 1$

$L = 2, \; S = 1;$

$J = 1, 2, 3$

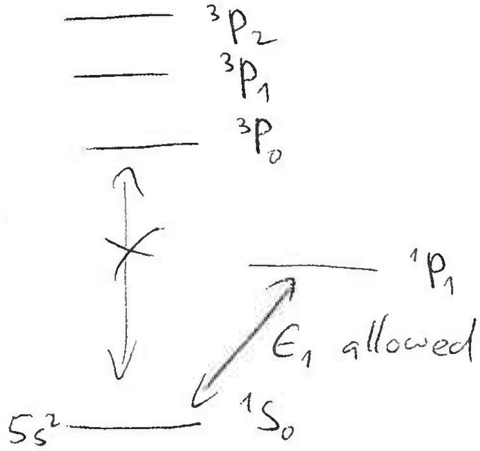
${}^3D_1, \; {}^3D_2, \; {}^3D_3$

${}^1D_2$

$L = 2, \; S = 0$

$J = 2.$

c).



the only E1 allowed ~~transition~~ transition is from ${}^1P_1$ down to the ground state. Hence, this level will be shortest lived.

d) We know that if $J \leq I$ we get splitting into $2J+1$; otherwise into $2I+1$.

${}^{81}Sr$, ${}^1P_1$ $\quad J = 1 \rightarrow$ splitting into 2 states,

means that $2I + 1 = 2 \Rightarrow I = \frac{1}{2}$

${}^{87}Sr$ $\quad {}^1P_1$ $\quad J = 1 \longrightarrow$ splitting into 3 states, means

$I > 1$

e). Dy: $[Xe]\,6s^2 4f^{10}$

$l = 3$ 10 f electrons equivalent to 4 f electr

Highest spin: $\uparrow\ \uparrow\ \uparrow\ \uparrow$ $S = 2$

m_l: 3 2 1 0

Highest L: $3 + 2 + 1 + 0 = 6$ $L = 6$

^5I

Orbital more than $\frac{1}{2}$ full:

$J = 4, 5, 6, 7, 8$

Highest J lowest:

$^5I_8$