

Structure of Matter

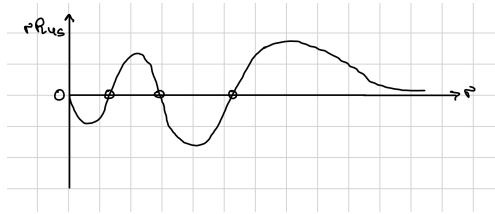
Midterm 1 Solutions - March 2024

Problem 1: One-electron wave functions

a) Sketch the radial part of the 4s wave function (rR_{4s}). Explain your answer (6 points).

To sketch the radial part of the 4s ($n = 4, l = 0$) wavefunction, we have to consider the following points:

- Starts at 0
- By convention, the first slope is always negative.
- The number of nodes (for a radial wavefunction) is given by $n - l - 1 = 4 - 0 - 1 = 3$.
- The amplitude and width should increase from the first slope to the last.
- Exponential decay to 0 as $r \rightarrow \infty$



b) The 4s and 5p radial wave functions have the same number of nodes. Which one is stronger bound? What is the binding energy? (7 points).

The 4s wavefunction is stronger bound due to its smaller principal quantum number. The binding energy for Hydrogen-like systems is given as follows:

$$E_{bin} = 13.6 \text{ eV} \frac{Z^2}{n^2} \quad (1)$$

For the $Z = 1$ case, we have the following result for the 4s wavefunction:

$$E_{bin,4s} = \frac{13.6 \text{ eV}}{4^2} = 0.85 \text{ eV} \quad (2)$$

For the 5p wavefunction, we have:

$$E_{bin,5p} = \frac{13.6 \text{ eV}}{5^2} = 0.544 \text{ eV} \quad (3)$$

The binding energy is the amount of energy that we need to put into the system to release the electron from that state. The 5p state has a smaller value and is therefore less bound than the 4s state.

c) To which states can an electron in the 4s state of hydrogen decay? (6 points).

It can decay to 3p and 2p. From the selection rules, we need the parity to change so decays to s or d orbitals are not allowed, and the photon can give or take $\Delta l = \pm 1$. "Forbidden" transitions do occur, but with rates smaller by several orders of magnitudes.

d) What will be the binding energy of a 4s electron in hydrogen-like mercury (Hg^{79+})? (6 points).

We use the binding energy equation given as follows:

$$E_{bin} = 13.6 eV \frac{Z^2}{n^2} \quad (4)$$

The value of Z is $79 + 1 = 80$ since the total charge is $+79$ and we have only one electron with -1 for this Hydrogen-like case ($Q = N_p - N_e = 80 - 1 = 79$). Therefore there are a total of 80 protons. For the 4s electron, we have $n = 4$:

$$E_{bin} = 13.6 eV \frac{80^2}{4^2} = 5440 eV \quad (5)$$

Problem 2: Fine structure

a) The fine structure levels are characterized by the quantum number j . What are the values of a 4f electron? (4 points).

A 4f electron has $s = 1/2$ and $l = 3$ (s, p, d, f, g, ...). The possible j values are given as $j = |l - s|, \dots, l + s$ (integer steps). Therefore, we have $j = 5/2, 7/2$.

b) Calculate the energy of the fine structure levels w.r.t. the unperturbed 4f energy.
Hint: $V_{SO} = \frac{A}{2}(j(j+1) - l(l+1) - s(s+1))$. The fine structure constant $A = 8 [cm^{-1}]$. (9 points).

The energy of the fine structure levels with respect to the original 4f energy is given by:

$$V_{SO} = \frac{A}{2}(j(j+1) - l(l+1) - s(s+1)) \quad (6)$$

For the $j = 5/2$ state, we have:

$$V_{SO,5/2} = \frac{8}{2} \left(\frac{5}{2} \left(\frac{5}{2} + 1 \right) - 3(3+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) = -16 \text{ cm}^{-1} \quad (7)$$

For the $j = 7/2$ state, we have:

$$V_{SO,7/2} = \frac{8}{2} \left(\frac{7}{2} \left(\frac{7}{2} + 1 \right) - 3(3+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right) = 12 \text{ cm}^{-1} \quad (8)$$

c) The shift of the levels is asymmetric w.r.t. the 4f energy. Show that conservation of energy is not violated. (6 points).

The two states have a degeneracy given by $g_j = 2j + 1$ which means that all of their levels contribute to taking away or giving energy from the initial 4f state. For $j = 5/2$, the degeneracy is 6 and for the $j = 7/2$, it is 8. The total energy shift is:

$$\Delta E = g_{5/2} V_{SO,5/2} + g_{7/2} V_{SO,7/2} = 6(-16 \text{ cm}^{-1}) + 8(12 \text{ cm}^{-1}) = -96 + 96 = 0 \quad (9)$$

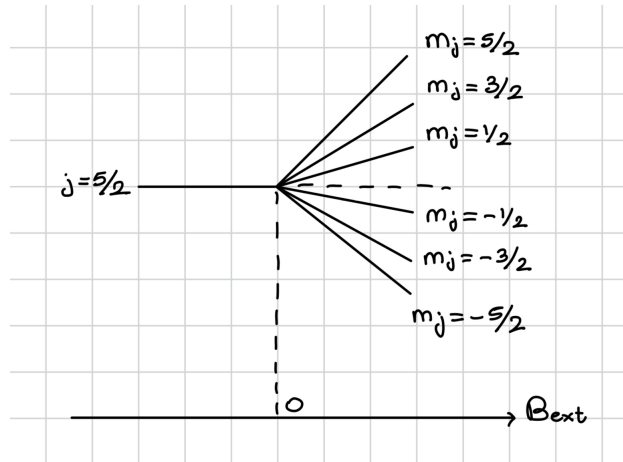
Therefore, energy is conserved.

d) Consider the lowest, strongest bound level. This system is put in an external magnetic field B . Sketch the behavior of the binding energies of the relevant states as a function of B . (6 points).

The lowest level is $j = 5/2$. Placing this system into an external magnetic field will cause the Zeeman effect to take place. The energy of this splitting from the original state is given as follows:

$$\Delta E = g_j \mu_B B_{ext} m_j \tag{10}$$

The splitting depends on the values of m_j which are given as $-5/2, -3/2, -1/2, 1/2, 3/2, 5/2$ (satisfying the degeneracy of 6 found earlier). The larger the value of m_j and B_{ext} , the greater the splitting.



Problem 3: Many-electron systems

a) To calculate energies and wave functions of many-electron atoms several approximations are made. Describe briefly the main assumption(s) underlying The Independent Particle Model and indicate what this implies for the representation of the wave function. (9 points).

The Independent Particle Model states that we can treat each electron in the system as a particle moving independently in an average potential given by the overall effect of the nucleus and the other electrons.

In this approximation, the overall wavefunction can be written as an antisymmetrised product of all individual one-electron wavefunctions:

$$\Psi_{tot} = \det|\psi_1\psi_2\dots\psi_n| \quad (11)$$

and the Hamiltonian can be written as a sum of all individual one-electron Hamiltonians:

$$H_{tot} = \sum_i h_i \quad (12)$$

Consider Mn^{6+} . The ionization potential of Mn^{6+} is 119.2 eV and its electronic configuration is $[\text{Ar}]3d$.

b) Calculate the effective nuclear charge experienced by the 3d electron. (7 points).

We can use the equation for the binding energy:

$$E_{bin} = 13.6 \text{ eV} \frac{Z_{eff}^2}{n^2} \quad (13)$$

We can deduce the binding energy from the ionisation potential and solve for the effective nuclear charge experienced by this 3d electron with $n = 3$:

$$Z_{eff} = n \sqrt{\frac{E_{bin}}{13.6 \text{ eV}}} = 3 \sqrt{\frac{119.2 \text{ eV}}{13.6 \text{ eV}}} \approx 8.88 \quad (14)$$

c) Why isn't the effective charge equal to 7+? Explain your answer. (7 points).

One might assume the outer electron experiences the full repulsion from all inner electrons on top of the attraction from the nucleus, which would indeed correspond to $Z_{eff} = 7$. However, since the electron wavefunctions extend radially, there is probability that the 3d electron is found closer to the nucleus than its average radius, where it feels a larger attraction to the nucleus and where there are fewer electrons between it and the nucleus. Hence, $Z_{eff} > 6+$.

The ground electronic configuration of U^{4+} is $[Rn]5f^2$.

d) Determine all allowed terms. Explain your answer. (10 points).

There are 2 equivalent electrons in the same orbital with $l_1, l_2 = 3$ and $s_1 = s_2 = 1/2$.

The possible L values are $L = |l_1 - l_2|, \dots, l_1 + l_2 = 0, 1, 2, 3, 4, 5, 6$.

The possible S values are $S = |s_1 - s_2|, \dots, s_1 + s_2 = 0, 1$.

Since there are 2 equivalent electrons, we need to consider the Pauli exclusion principle that does not allow them to have the exact same set of quantum numbers. Therefore, the allowed states have $L + S = \text{even}$.

For $S = 0$, only even L are allowed, so we have $L = 0, 2, 4, 6$ and the terms from here are $^1S, ^1D, ^1G, ^1I$.

For $S = 1$, only odd L are allowed, so we have $L = 1, 3, 5$ and the terms from here are $^3P, ^3F, ^3H$.

d) Which term is the ground term? Explain your answer. (7 points).

The lowest term can be identified with Hund's rules:

1. The term with the largest $2S + 1$ (largest multiplicity) lies lowest. So we consider only the $^3P, ^3F, ^3H$ terms.
2. If there are several terms with maximal multiplicity, the term with largest L lies lowest. So the ground term is 3H .
3. (If the unfilled subshell is *less than half full*, the level with the *lowest* J has the lowest energy. If the unfilled subshell is *more than half full*, the level with the *highest* J has the lowest energy. The allowed J values are $J = 0, 2, 4, 6$. In this case, the f orbital is less than half-filled since it can take 14 electron so the ground level is 3H_6 .)

Consider Ir, of which the electronic configuration is: $[\text{Xe}]6s^2 4f^{14} 5d^7$.

f) Determine the ground term and ground level of Ir. Explain your solution steps. (10 points).

There are 7 electrons in the d orbital that can take 10 so we can consider the case of 3 electrons. We have $l_1 = l_2 = l_3 = 2$ and $s_1 = s_2 = s_3 = 1/2$.

The d orbital is more than half filled so we need the highest J to find the ground term and level as well as maximum multiplicity and largest L (Hund's Rules). The maximum value of S is $3/2$ when all 3 electrons have a spin in the same direction.

Since we consider the case of maximum S and same m_s , the 3 electrons need to have a different value of m_l to satisfy the Pauli exclusion principle. The d orbital allows $l = 2$ and $m_l = 2, 1, 0, -1, -2$. For the maximum M_L we need $M_L = m_{l_1} + m_{l_2} + m_{l_3} = 2 + 1 + 0 = 3$. This corresponds to $L = 3$. We can deduce the ground term as 4F .

The allowed J values for $S = 3/2$ and $L = 3$ are $J = 3/2, 5/2, 7/2, 9/2$. Since we have a more than half-filled orbital as mentioned before, the largest J has the lowest energy. Therefore, the ground level is $^4F_{9/2}$.