

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE : PHAS2224

**ASSESSMENT : PHAS2224A
PATTERN**

MODULE NAME : Atomic and Molecular Physics

DATE : 07-May-09

TIME : 10:00

TIME ALLOWED : 2 Hours 30 Minutes

Answer ALL SIX questions from Section A and THREE questions from Section B.

The following data may be used if required:

Speed of light, $c = 2.998 \times 10^8 \text{ ms}^{-1}$

Planck constant, $h = 6.626 \times 10^{-34} \text{ Js}$

Mass of a nucleon (proton or neutron), $m_u = 1.66 \times 10^{-27} \text{ kg}$

Bohr radius, $a_0 = 0.529 \times 10^{-10} \text{ m}$

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

Section A: Answer ALL SIX questions.

1. The configuration of an atom is given as $1s^22s^22p^2$. Explain each term in this expression and state the associated quantum numbers. [4]
How many electrons are required to fill a shell with quantum number n ? [1]
How many electrons are required to fill a sub-shell with quantum number l ? [1]
How many electrons need to be added to the above configuration for all shells to be closed? [1]
Give the corresponding closed shell configuration. [1]
2. State the Pauli Exclusion Principle in the context of multielectron atoms. What condition does it place on the symmetry of the total wavefunction of the system? [4]
Why is the ground-state of helium a spin singlet? [3]
3. State Hund's rules for the ordering of terms in increasing energy according to their value of S , L and J . [6]
4. Describe the three processes that may occur when a two-level system interacts with a radiation field. For each process, indicate the properties of the photon(s) involved. You may use diagrams to answer this question. [6]
5. State the electric dipole selection rules for the quantum numbers J , M_J and S for a multi-electron atom. [4]
Hence explain why the $1s2s$ (3S) excited state of helium is metastable. [4]
6. The energy of an ideal diatomic molecule may be approximated as

$$E \simeq E_{\text{electron}}(R_e) + BJ(J+1) + \left(v + \frac{1}{2}\right) \hbar\omega.$$

Explain what each of the terms in the approximation represents, and define the symbols B , J , v and ω . [5]

When is this approximate expression for the energy valid? [1]

Section B: Answer THREE questions.

7. (a) Distinguish between elastic and inelastic collisions, and between total (σ_T) and differential ($d\sigma/d\Omega$) cross-sections. [4]
- (b) In the context of atomic collisions, state:
- i. what is meant by "threshold energy", giving an example [2]
 - ii. the relationship between σ_T and $d\sigma/d\Omega$ which exists below the lowest threshold energy. [2]

Use this relationship to find an expression for σ_T if $d\sigma/d\Omega = a \cos^8 \theta$ (where a is a constant). [4]

- (c) Derive an expression (the Beer-Lambert law) for σ_T which enables its determination by measuring the attenuation of a projectile beam of particles of type A incident on a slab of material containing target particles B, defining all symbols. [6]

A beam of positronium atoms traverses a cell of length 40 mm containing a gas of number density $5 \times 10^{19} \text{ m}^{-3}$ with the result that the positronium beam intensity is halved. Work out the total cross-section for this process in units of πa_0^2 . [2]

8. (a) Briefly explain the physical origin of the spin-orbit interaction and why the associated energy splitting takes the form of the equation below: [9]

$$\Delta E = \frac{1}{2} A(L, S)[J(J+1) - L(L+1) - S(S+1)]$$

- (b) By considering the difference in spin-orbit energies between two adjacent levels of the same term, show that this quantity is proportional to the larger of the two J values (Landé interval rule). [3]
- (c) Tabulate the possible values of J for the 3P state of magnesium and draw a level diagram for this term. [8]

9. (a) The allowed energies of the electron in the hydrogen atom are given by the equation

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

where n is a positive integer. State, and qualitatively justify, how the above equation may be modified to express the energy levels E_{n_l} of an alkali metal atom in terms of an effective nuclear charge and the quantum defect. [4]

The quantum defect for the 3s state of sodium is 1.37. Calculate in eV the ionization energy of this state. [2]

- (b) When a high- Z element is bombarded with sufficiently energetic electrons the emission of X-rays is observed.

i. Explain the form and general features of the X-ray spectra observed in terms of the underlying atomic processes that are occurring when the electrons interact with the target. [4]

ii. Describe and explain the change in the X-ray emission spectrum when the target element is changed. [1]

iii. Describe and explain the change in the X-ray emission spectrum when the electron energy is increased. [1]

- (c) The characteristic lines in the X-ray spectrum are given by the equation:

$$\frac{1}{\lambda} = R(Z - S)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

i. Explain the meaning of each of the terms in this equation. [2]

ii. State the values of n_i and n_f for the X-ray lines labelled as K_β . [2]

iii. Explain the reason for the inclusion of the screening constant, S . [1]

iv. Calculate the frequency ratio of the K_β transition lines of bismuth ($Z = 83$) and tungsten ($Z = 74$). [3]

10. The Hamiltonian for an atom in a magnetic field \underline{B} is

$$H = H_0 + H_{LS} + H_B,$$

where H_0 is the unperturbed Hamiltonian and H_{LS} and H_B are small corrections due to the spin-orbit interaction and the Zeeman effect respectively.

- (a) Describe the physical mechanism of how the Zeeman interaction of an atom with an external magnetic field modifies the energy level structure of the atom. Your answer should discuss the limiting cases $H_{LS} \gg H_B$ and $H_{LS} \ll H_B$, in each case stating the good quantum numbers. [9]
- (b) Give a formula for the potential energy V_B arising from the interaction of a general magnetic moment $\underline{\mu}$ with a magnetic field \underline{B} . [1]
- (c) Give an expression for the magnetic moment, $\underline{\mu}_L$, associated with the orbital angular momentum \underline{L} of an electron, in terms of \underline{L} , the Bohr magneton μ_B and a g-factor g_L . Do the same for the spin magnetic moment $\underline{\mu}_S$, in terms of \underline{S} , μ_B and g_S . [2]
- (d) Derive a formula for the interaction energy between the total magnetic moment and a magnetic field \underline{B} in terms of the projection quantum numbers M_L and M_S . Assume that the interaction with the magnetic field is substantially larger than any spin-orbit interaction. You may take $g_L = 1$ and $g_S = 2$. [3]
- (e) Sketch the energy level structure for atomic hydrogen in the excited 3d configuration when the atom is exposed to a magnetic field. Assume that the interaction with the magnetic field is weak compared to the spin-orbit coupling. Label each of the levels in the magnetic field with the appropriate m_j value. You will need to refer to the formula below for the Landé g-factor in order to determine which multiplet has the larger splitting. [5]

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

11. (a) The Hamiltonian for the H_2^+ molecular ion can be written in atomic units as

$$H(\underline{r}, \underline{R}) = -\frac{\nabla_{\underline{R}}^2}{M_p} - \frac{\nabla_{\underline{r}}^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

where \underline{R} is the internuclear vector, \underline{r} is the position vector of the electron, r_A and r_B are the distances between the electron and nuclei A and B respectively, and M_p is the mass of a proton.

- i. Explain what each of the 5 terms in this Hamiltonian represents. [3]
 - ii. Write down Schrödinger equations for electronic and nuclear motion in the Born-Oppenheimer approximation. [4]
 - iii. In writing the electronic Schrödinger equation in the Born-Oppenheimer approximation, which terms are neglected? [1]
- (b) Briefly outline the physical basis of the Franck-Condon principle and how it relates to the distribution of final vibrational states in transitions between molecular electronic states. Your answer should include an expression for the Franck-Condon factor in terms of the initial and final vibrational wavefunctions. [3]

THIS QUESTION CONTINUES ON THE NEXT PAGE.

- (c) Figure 1 shows parts of the potentials of the ground electronic state and an excited electronic state of a homonuclear diatomic molecule. In both cases only the lowest parts of the potential wells are shown, together with the lowest few vibrational levels in each state.

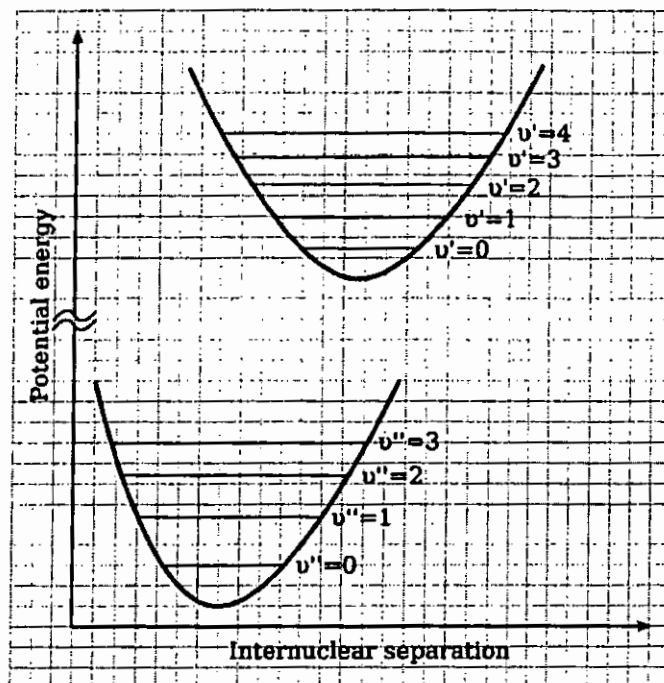


Figure 1: For use with question 11.

- i. In the UV absorption spectrum for excitation from $v'' = 0$ in the ground state, to which final vibrational level of those shown will the strongest transition occur? In the UV emission spectrum for $v' = 0$ in the excited electronic state, to which final vibrational level of those shown will the strongest transition occur? Briefly explain your reasoning in both cases. [4]
- ii. In the UV absorption spectrum corresponding to an initial state of $v'' = 0$, a series of lines is observed. The two lowest frequency lines have a spacing of 160 cm^{-1} . Given that the molecule is $^{79}\text{Br}_2$, calculate the spring constant of the molecule in the electronically excited state. You should assume that the excited electronic state potential is well described by a harmonic oscillator. [5]

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE : **PHAS2224**

ASSESSMENT : **PHAS2224A**
PATTERN

MODULE NAME : **Atomic and Molecular Physics**

DATE : **12-May-10**

TIME : **14:30**

TIME ALLOWED : **2 Hours 30 Minutes**

Answer ALL SIX questions from Section A and THREE questions from Section B.

The following data may be used if required:

Planck constant, $h = 6.626 \times 10^{-34}$ Js

Speed of light, $c = 2.998 \times 10^8$ ms⁻¹

Mass of an electron, $m_e = 9.11 \times 10^{-31}$ kg

Mass of a nucleon (proton or neutron), $m_u = 1.66 \times 10^{-27}$ kg

Bohr radius, $a_0 = 0.529 \times 10^{-10}$ m

Bohr magneton, $\mu_B = 9.274 \times 10^{-24}$ JT⁻¹

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

Section A: Answer ALL SIX questions.

1. Outline the Rutherford scattering experiment, explaining what was measured and the significance of the results with respect to the structure of the atom. [7]
2. Write down the expression showing the proportionality between the energy E_n for a level of the hydrogen atom and the principal quantum number n . [1]
From the expression, deduce the Rydberg formula for the wavelength of the photon absorbed when an electron makes a transition from a state n to one with quantum number $m > n$. [4]
Hence give the expression for the wavelength of the photon required to ionise the atom from the state n . [2]
3. Define the *reduced mass* of a system of particles, and write down an expression for the reduced mass, μ , of a system containing two particles of mass M and m . [3]
Calculate the reduced mass of positronium. [3]
4. When a high- Z element is bombarded with sufficiently energetic electrons the emission of X-rays is observed. Briefly explain the form and general features of the X-ray spectra observed in terms of the underlying atomic processes that are occurring when the electrons interact with the target. [4]
Describe the change in the X-ray emission spectrum when the target element is changed. [1]
Describe the change in the X-ray emission spectrum when the electron energy is increased. [1]

5. State Fermi's golden rule for transitions between quantum states induced by electromagnetic radiation and hence state what is meant by "allowed" and "forbidden" transitions. [4]

Explain what is meant when an atomic energy level is described as "metastable". [2]

State how the lifetime of an energy level is related to the linewidth for spontaneous emission from that energy level. [1]

6. Indicate which of the following molecules you expect to be well described as ionically bonded, and which you expect to be well described as covalently bonded:



[2]

State what type of transitions in an ideal diatomic molecule gives rise to absorption lines in the microwave region of the electromagnetic spectrum, and hence which molecules will have a microwave absorption spectrum. [2]

Which of the molecules above will absorb energy in the microwave region of the electromagnetic spectrum? [1]

Under what circumstances do you expect the rigid rotor model of a diatomic molecule to be applicable? [1]

State the selection rule for the rotational quantum number J for rotational transitions in diatomic molecules. [1]

Section B: Answer THREE questions.

7. (a) Explain what is meant by the “radial probability density” of the hydrogen atom wavefunction. [2]
- (b) The ground (1s) state of hydrogen has the radial wavefunction

$$R_{1s}(r) = \frac{1}{\sqrt{a_0^3\pi}} \exp(-r/a_0).$$

Sketch the radial probability density of the ground state, $P_{1s}(r) = 4\pi r^2 |R_{1s}(r)|^2$, and mark on your sketch the mean radius and most probable radius for finding an electron. [4]

- (c) For a state with principal quantum number, $n > 1$, what are the possible values of the orbital angular momentum quantum number, l ? [2]
- (d) For the state with orbital angular momentum l , what are the possible values of the magnetic quantum number m_l ? [2]
- (e) What further quantum numbers (if any) are required to completely specify the state of the electron in the hydrogen atom? [2]
- (f) From the form of the spherical harmonic function $Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$, what can be said about the angular probability distribution of the ground state of the hydrogen atom? [2]
- (g) Given that the number of peaks in the radial probability distribution P_{nl} is $n - l$, sketch the radial probability distributions for all the orbitals in the $n = 2$ state of hydrogen. [6]
8. (a) Explain the notation of the Russell-Saunders energy level (fine structure term) symbol:

$$^{2S+1}L_J.$$

- [3]
- (b) When determining the term from a given electronic configuration which electrons must be considered and which may be neglected? Explain why. [2]
- (c) State Hund’s Rules for the ordering of terms in increasing energy according to their value of S , L and J . [6]
- (d) What restriction is placed on the symmetry of the wavefunction of a multi-electron atom by the Pauli Exclusion Principle? [2]
- (e) Explain *qualitatively* how the Pauli Exclusion Principle gives rise to the ordering of terms according to their value of S described by Hund’s Rules. [4]
- (f) Tungsten (W) has electronic configuration $[\text{Xe}]5d^46s^2$. The ground state has total spin $S = 2$ and total orbital angular momentum $L = 2$. What values of J are possible? Hence write down the lowest energy term of the ground state. [3]

9. (a) Give an expression for the magnetic moment, $\underline{\mu}_L$, associated with the orbital angular momentum \underline{L} of an electron, in terms of \underline{L} , the Bohr magneton μ_B and a Landé g -factor g_L .

Do the same for the spin magnetic moment $\underline{\mu}_S$, in terms of \underline{S} , μ_B and g_S . [2]

- (b) Derive a formula for the interaction energy between the *total* magnetic moment and an external magnetic field \underline{B} in terms of the quantum numbers m_l and m_s in the strong field limit. (You may take $g_L = 1$ and $g_S = 2$). [6]

How many values does this interaction energy take for neutral copper in its ground state $^2S_{1/2}$? [2]

- (c) Describe briefly the physical mechanism of the anomalous Zeeman effect in the weak field limit. Identify the good quantum numbers in this case. [3]

- (d) The ground state oxygen atom has the configuration $1s^2 2s^2 2p^4$ and the lowest energy term symbol is 3P .

i. Deduce into how many *energy levels* (fine structure terms) the 3P term is split by the spin-orbit interaction, and give the corresponding possible values of J . Indicate which energy level has the lowest energy. [3]

ii. Draw a diagram showing the splitting of the lowest energy level when the oxygen atom is placed in a weak magnetic field of strength 0.2 T. Clearly indicate the energy level splitting in the diagram in terms of the magnetic field B . You will need to use the following formula for the Landé g -factor. [4]

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

10. (a) With reference to diagrams of a two-level system, explain the three processes that may occur when the system interacts with a radiation field. For each process, discuss the properties of the photon(s) involved. [6]

(b) Explain what is meant by the term “population inversion”, and why it is needed for LASER action. Explain why it is not possible to obtain a population inversion in a two level system. [4]

(c) Explain, with the aid of a diagram, how LASER action may be achieved in a 3 level system. [5]

(d) For each of the following atomic transitions, state which are allowed by the dipole selection rules, and which are forbidden. Explain your answers in terms of the quantum numbers involved and the relevant selection rules.

i. $^1P_1 \rightarrow ^1S_0$

ii. $^1P_1 \rightarrow ^3P_2$

iii. $^3D_0 \rightarrow ^3P_0$

iv. $^1P_1 \rightarrow ^1F_0$

v. $^4D_1 \rightarrow ^4F_1$ [5]

11. (a) The Hamiltonian for the H_2^+ molecular ion can be written in atomic units as

$$H(\underline{r}, \underline{R}) = -\frac{\nabla_{\underline{R}}^2}{M_p} - \frac{\nabla_{\underline{r}}^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

where \underline{R} is the internuclear vector, \underline{r} is the position vector of the electron, r_A and r_B are the distances between the electron and protons A and B respectively, and M_p is the mass of a proton.

- i. Explain what each of the 5 terms in this Hamiltonian represents. [3]
 - ii. Write down Schrödinger equations for electronic and nuclear motion in the Born-Oppenheimer approximation. [4]
 - iii. In writing the electronic Schrödinger equation in the Born-Oppenheimer approximation, which terms are neglected? [1]
- (b) The electronic wavefunctions for the H_2^+ molecular ion may be approximated by taking a linear combination of hydrogen atom 1s orbitals located on each proton as:

$$\psi_{\pm}(r_a, r_b, R) = \frac{1}{\sqrt{2}} [\phi_{1s}(r_a) \pm \phi_{1s}(r_b)]$$

Comment on the probability of finding the electron on each proton when $|R| = \infty$, and so explain the choice of the coefficients appearing in this linear combination [3]

State which combination is energetically stable and briefly explain why. [1]

Sketch the form of the symmetric and antisymmetric wavefunctions and their corresponding probability densities. [4]

- (c) Calculate an approximate dissociation energy of LiF given that the ionization potential of lithium is 5.39 eV, the electron affinity of F is 3.45 eV, and the equilibrium internuclear separation of LiF is 1.56 Å. [Note: 1 Hartree (1 atomic unit of energy) = 27.2 eV] [4]

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE : **PHAS2224**

ASSESSMENT : **PHAS2224A**
PATTERN

MODULE NAME : **Atomic and Molecular Physics**

DATE : **20-May-11**

TIME : **14:30**

TIME ALLOWED : **2 Hours 30 Minutes**

Answer ALL SIX questions from Section A and THREE questions from Section B.

The following data may be used if required:

Mass of an electron, $m_e = 9.11 \times 10^{-31}$ kg

Fundamental electronic charge, $e = 1.602 \times 10^{-19}$ C

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

Section A: Answer ALL SIX questions.

1. A quantum particle is elastically scattered by an atom. At large distances from the target, the wavefunction takes the form

$$\psi(\underline{r}) = e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r}.$$

Explain the physical significance of the two terms on the right-hand side, defining k and $f(\theta, \phi)$. [4]

How is the above modified in the case of excitation? [3]

2. Ignoring electron spin, the bound states of the hydrogen atom are described by the quantum numbers n, l, m_l . Explain their significance and state their possible values. [5]
What additional quantum numbers are required when electron spin is incorporated and what values can they take? [2]
3. In the context of many-electron atoms, explain what is meant by LS - and jj -coupling, referring to the significance of the spin-orbit interaction in determining their relative importance. [6]
4. Explain how X-ray emission may be produced from atomic targets. [2]
Briefly explain the main characteristics of the X-ray spectra so produced. [5]
5. What are the necessary requirements to achieve LASER action? [3]
Give one example of a specific system which exhibits LASER action, showing how it meets these requirements. [4]
6. Discuss briefly the two main types of bonding found in diatomic molecules and explain the interactions which lead to this bonding. [4]
Give one example molecule for each type of bonding. [2]

Section B: Answer THREE questions.

7. Sketch a diagram of Thomson's cathode ray experiment, indicating the key components. [4]

Explain *quantitatively* how this experiment led to the determination of the charge-to-mass ratio (e/m) of the electron, deriving explicit formulae for the relevant measured quantities. [10]

How did Thompson demonstrate that the observed particles were fundamental to all matter? [2]

Deduce a formula which shows how the *angular* deflection of the electron beam depends on e/m and compute its value for a magnetic flux density of 0.001 T and an electric field strength of 10,000 V/m, both extending over 0.05 m of the beam path. [4]

8. By considering the probability density $|\psi(1,2)|^2$ with respect to exchange of two indistinguishable particles (1,2), explain what is meant by *symmetric* and *antisymmetric* wavefunctions. [3]

If α and β represent one-electron spin wavefunctions, show that the two-electron spin wavefunctions:

$$\chi^{(T)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \quad \text{and} \quad \chi^{(S)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

are respectively symmetric ($\chi^{(T)}$) and antisymmetric ($\chi^{(S)}$) under exchange of labels. [2]

What condition does the Pauli Exclusion Principle (PEP) place on the symmetry of the total wavefunction of a system of identical fermions? [2]

Which two-electron spin wavefunction represents the ground state of the helium atom? Justify your answer with reference to the PEP and the spatial part of the wavefunction, and give the Russell-Saunders ($^{2S+1}L_J$) level symbol. [8]

The element boron (B) has atomic number 5. Write down the electron configuration of the ground state of its ion B^+ and deduce the electronic spin wavefunction. [3]

Explain why the first excited state of B^+ is expected to have a metastable component. [2]

9. Consider the three types of spectra that can be observed for a diatomic molecule such as HF. What types of motion give rise to each of these spectra? [3]

At what wavelengths do each of these spectra typically occur? [3]

What selection rules govern the allowed transitions for each spectral type? [5]

A cold sample of a diatomic molecule is found to absorb infrared radiation at 2584.8, 2605.3, 2644.8, 2663.5 and 2681.6 cm^{-1} . Identify the transitions observed in this spectrum and give quantum numbers for the initial and final states involved. [6]

Briefly explain what information can be obtained from these transitions. [3]

10. State, without proof, a formula in atomic units (a.u.) for the energy levels, E_{nl} , of an alkali metal atom in terms of an effective nuclear charge Z_{eff} , the principal quantum number n , and the quantum defect Δ_{nl} . [3]

State and qualitatively explain how Δ_{nl} varies with the quantum numbers n and l . [5]

The quantum defect for the 4s state of potassium is 2.19. Calculate in a.u. the ionization energy of this state. [2]

Give the selection rules which control dipole allowed transitions in an atom such as K. [5]

A K atom is in a 2S state in which the spin-orbit coupling is weak enough to be neglected. State, with reasons, whether you would expect it to undergo a dipole allowed transition to states with the following symmetry

(a) 2S

(b) $^2P^o$

(c) 2D

(d) 4S

(e) $^4P^o$ [5]

11. Define the angular momentum quantum numbers S , L and J of a many-electron atom. [3]

Explain how the structure of the energy levels of a many-electron atom for which S , L and J are all non-zero is modified in the presence of:

(a) A weak magnetic field,

(b) A strong magnetic field,

(c) An electric field. [6]

Explain what determines whether a magnetic field can be regarded as "weak" or "strong". [2]

In the absence of a magnetic field, a sodium atom in the $4^2D_{3/2}$ state undergoes a transition to the $3^2P_{1/2}$ state by emitting a photon of energy E . What energy photons will be emitted in the presence of a weak magnetic field of strength B ? You may assume: [9]

$$g_J = 1 + \left(\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right)$$



Answer ALL SIX questions from Section A and THREE questions from Section B.

The following data may be used if required:

Planck constant, $h = 6.626 \times 10^{-34}$ Js

Rydberg constant, $R=109677.58$ cm⁻¹

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

Section A: Answer ALL SIX questions.

1. Explain what is meant by the words *configuration*, *term* and *level* when describing the states of atoms. Illustrate your answer by considering the ground state of the carbon atom. [6]
2. A collection of two-level atoms is illuminated by a radiation field. What processes occur which transfer population between the ground state and excited state (and vice versa). [3]
What conditions must the ground and excited state populations satisfy in order to make a laser? Why is this not possible in a two-level system? [4]
3. Explain how lasers can be used to cool atoms. [6]
4. An atom of spin S and electron orbital angular momentum L interacts with a magnetic field B. Explain how the energy levels of this atom will split if the field is (a) weak and (b) strong. What determines whether the field is weak or strong? [7]
5. Define the *reduced mass* of a system of particles. Write down an expression for the reduced mass, μ , of a system comprising a particle of mass m_1 and a particle of mass m_2 . [4]
Positronium is a quasi-atom composed of an electron and a positron which have equal mass (m_e). Calculate the reduced mass of positronium. [2]
6. Write down the selection rules which govern electric dipole transitions from the ground state of the helium atom. Hence explain why the first excited state of helium is metastable. [8]

Section B: Answer THREE questions.

7. The energy levels of an ideal diatomic molecule may be approximated by

$$E \approx E_{\text{electron}}(R_e) + BJ(J + 1) + (v + \frac{1}{2})\hbar\omega.$$

Explain what each of the terms in the approximation represents, and define the symbols B , J , v and ω . [5]

When is this approximation valid? [2]

Describe and sketch the appearance of the spectrum produced by transitions between rotational states of the ideal diatomic molecule. In which region of the electromagnetic spectrum do the transitions occur? [6]

Rotational spectroscopy of the HF molecule produces a spectrum where the line spacing is 1258500 MHz. Estimate the bond length of HF. You can take the mass of atomic H and atomic F to be 1.673×10^{-27} kg and 31.52×10^{-27} kg respectively. What are the major sources of error in this estimate? [7]

8. State the Pauli Principle as it applies to the wavefunction of a system with two electrons. Demonstrate how this leads to exclusion for electrons with identical quantum numbers. [4]

If α and β represent one-electron spin wavefunctions, two possible two-electron spin wavefunctions can be written:

$$\chi^{(T)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1)) \text{ and } \chi^{(S)} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1)).$$

For each of these functions, determine its symmetry under exchange of electrons. Write down two more two-electron spin wavefunctions which are *symmetric* under exchange. [6]

Give the electron configuration for an excited helium atom for which one electron is promoted to a 2p orbital. Write down possible wavefunctions for this configuration with (a) symmetric and (b) anti-symmetric spin functions. Give the term symbol designation for each of these wavefunctions. Explain which of the terms you expect to be lower in energy. Give allowed levels for this term and suggest which level should lie lowest in energy. [10]

9. The optically active electron in an alkali metal atom can be characterised by quantum numbers n and l . Explain what is meant by these quantum numbers. What is meant when this electron is referred to as 'penetrating'? How does electron penetration affect the ordering of the energy levels in these atoms? [6]

The energy levels of a system with a single optically active electron can be represented by the formula:

$$E_{nl} = -R \frac{Z_{\text{eff}}^2}{(n - \Delta_{nl})^2}.$$

Carefully explain the meaning of the symbols and explain how you would expect Δ_{nl} to vary as a function of n and l . [6]

The ground configuration of doubly ionized boron (B^{2+}) is $1s^2 2s^1$. The ionization energy of the ground state measured as 303905 cm^{-1} ; and that for the $1s^2 3s^1$ state as 124703 cm^{-1} . Calculate the quantum defect for these two states. Estimate the ionization energy of the $1s^2 4s^1$ state. [8]

10. Explain how X-ray spectra are produced in an atomic sample. [2]

With the aid of a sketch explain the main features displayed in a typical X-ray spectrum. [4]

Moseley's Law states:

$$\nu = C(Z - S)^2.$$

Explain the terms in this expression and how it relates to the X-ray spectrum you have described. [6]

A line is designated K_α . Explain what this means. [2]

Use Moseley's Law to evaluate the ratio of wavelengths for K_α lines of zinc ($Z = 30$) and gold ($Z = 79$). [6]

11. Explain the physical basis of the spin-orbit interaction in atoms. [5]

The change in energy, ΔE , of an atomic state due to the spin-orbit interaction is

$$\Delta E = A(LS)[J(J + 1) - L(L + 1) - S(S + 1)],$$

where J , S and L are quantum numbers for the total angular momentum, the spin angular momentum and the orbital angular momentum of the atom. The energy $A(LS)$ is independent of J . Using this result derive the Landé interval rule. [5]

The ground state of iron has the configuration $3d^6 4s^2$ and the term 5D . Determine the possible J values and hence, assuming that for this term $A(L, S)$ has a magnitude of 94 cm^{-1} , give a level diagram for this term. [10]

UNIVERSITY COLLEGE LONDON

EXAMINATION FOR INTERNAL STUDENTS

MODULE CODE : PHAS2224

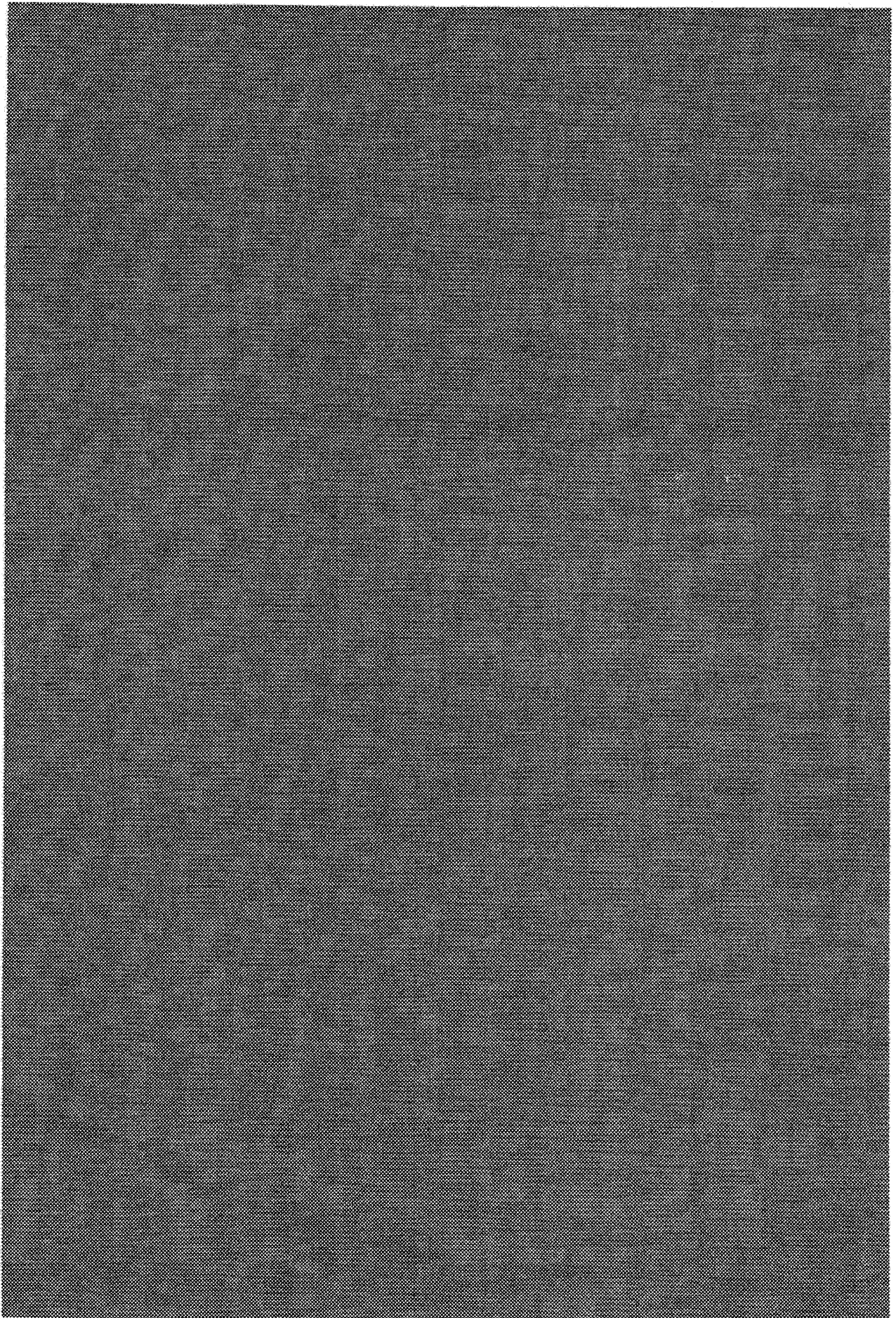
**ASSESSMENT : PHAS2224A
PATTERN**

MODULE NAME : Atomic and Molecular Physics

DATE : 24-Apr-13

TIME : 14:30

TIME ALLOWED : 2 Hours 30 Minutes



Answer ALL SIX questions from Section A and THREE questions from Section B.

The following data may be used if required:

Bohr Magneton, $\mu_B = 0.5 \text{ a.u.} = 0.467 \text{ cm}^{-1} \text{ T}^{-1}$

Mass of a proton, $M_p = 1.6726 \times 10^{-27} \text{ kg}$

Planck's constant over 2π , $\hbar = 1.0545 \times 10^{-34} \text{ Js}$

Rydberg constant, $R_\infty = 0.5 \text{ a.u.} = 109737.32 \text{ cm}^{-1}$

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

Section A: Answer ALL SIX questions.

1. How can an X-ray spectrum be produced in an atomic sample? [2]
With the aid of a sketch explain the main features displayed in a typical X-ray spectrum. [5]
2. A diatomic molecule such as NaCl absorbs light in three different wavelength regions. State what the regions are and the changes that give rise to the absorption of light. [6]
3. What are the necessary requirements to achieve laser action? Why is this not possible in a two-level system? [4]
Give one example of a specific system which exhibits laser action showing how it meets the requirements for laser action. [4]
4. A helium atom has the configuration $1s^1 3d^1$. Give the allowed terms and levels arising from this configuration. [7]
5. State the Pauli Principle as it applies to the wavefunction of a system with two electrons. Demonstrate how this leads to exclusion for electrons with identical quantum numbers. [4]
Write down an example of a space-spin two-electron wavefunction which satisfies the Pauli Principle and give it a spin state. [3]
6. What is hyperfine structure? How does it lead to the 21 cm in atomic hydrogen? [5]

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PLEASE TURN OVER

Section B: Answer THREE questions.

7. The bound energy levels of a hydrogen-like atom are given by the formula

$$E_n = -R_\infty \frac{Z^2}{n^2}.$$

Explain the meaning of each term in this formula. [4]

State, and qualitatively justify, how the above equation may be modified to express the energy levels E_{nl} of an alkali metal atom in terms of an effective nuclear charge and the quantum defect, Δ_{nl} . [5]

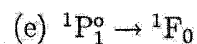
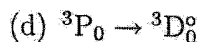
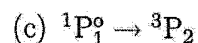
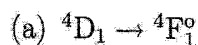
How would you expect the quantum defect to vary as a function of n and l ? [3]

A series of transitions in atomic potassium consists of emissions from several np levels to the $4s$ atomic ground state. Transitions are observed at 12985 cm^{-1} when $n = 4$, 24701 cm^{-1} when $n = 5$, and 28999 cm^{-1} when $n = 6$. The series limit, which can be assumed to be the same as the ionisation potential of the $4s$ level, is at 35010 cm^{-1} . Calculate the quantum defects of the $4p$, $5p$ and $6p$ levels. Hence estimate the wavenumber of the corresponding transition from the $n = 7$ level. [9]

8. Explain what is meant by the words *configuration*, *term* and *level* when describing the states of a many-electron atom. In each case illustrate your answer by an example. [6]

State the selection rules which control dipole-allowed transitions between states in a many-electron atom. Distinguish between those selection rules which are rigorous and those that are approximate. [6]

For each of the following atomic transitions, state which are allowed by the dipole selection rules, and which are forbidden. Explain your answers in terms of the quantum numbers involved and the relevant selection rules.



Place these transitions in approximate order of strength. [3]

9. The Hamiltonian for an atom in a magnetic field \mathbf{B} is

$$H = H_0 + H_{LS} + H_B,$$

where H_0 is the unperturbed Hamiltonian and H_{LS} and H_B are small corrections due to the spin-orbit interaction and the Zeeman effect respectively. Explain the origins of H_{LS} and H_B in terms of the interaction between a magnetic dipole moment and a magnetic field. [4]

What effect does each of these have on the energy levels of the atom? [2]

Comment on the limiting cases $H_{LS} \gg H_B$ and $H_{LS} \ll H_B$. [2]

With the aid of vector diagrams, illustrate the coupling of spin (\mathbf{S}) and orbital (\mathbf{L}) angular momentum in the limits above, for each case stating the good quantum numbers. [4]

In a zero magnetic field the highest and lowest energy levels of the $(4s^1 4p^1) {}^3P$ first excited state of magnesium are separated by 60 cm^{-1} . Calculate the separations of all the components of $(4s^1 4p^1) {}^3P$. [5]

Estimate the magnitude of an external magnetic field that would be considered strong in this case. [3]

10. State, giving your reasons, which of the following diatomic molecules would you expect to undergo dipole-allowed vibrational transitions (a) HCl, (b) H_2 , (c) CO. State the selection rules associated with such transitions. [6]

For many covalent diatomic molecules the effective potential in which the nuclei move is well described by the Morse potential:

$$V(R) = D_e (e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)})$$

Sketch the form of $V(R)$, marking clearly on your sketch the parameters D_e and R_e . Include also a sketch of a parabolic potential that approximates the Morse Potential near the potential minimum. [4]

Show that for small displacements from R_e the Morse potential is approximately harmonic (You may use the expression $e^{-ax} \simeq 1 - ax + \frac{1}{2}(ax)^2 \dots$ valid for small x). [3]

From your approximation to $V(R)$, find an expression for the spring constant, k , of the bond in terms of α and D_e . [2]

Given that for the hydrogen molecule H_2 , $D_e = 7.24 \times 10^{-19} \text{ J}$ and $\alpha = 1.93 \times 10^{10} \text{ m}^{-1}$, calculate the spring constant of the bond, and hence the photon frequency between vibrational levels near the bottom of the potential well. [5]

11. (a) Define the *reduced mass* of a system of particles. Write down an expression for the reduced mass, μ , of a system comprising a particle of mass m_1 and a particle of mass m_2 . [4]

Explain how the spectrum of

- i. a one-electron atom,
- ii. a rotating molecule,
- iii. a vibrating molecule,

depends on the reduced mass of the system. Explain which of these is the most sensitive to isotopic changes. [5]

- (b) The Hamiltonian for the H_2^+ molecular ion can be written in atomic units as

$$H(\underline{r}, \underline{R}) = -\frac{\nabla_{\underline{R}}^2}{M_p} - \frac{\nabla_{\underline{r}}^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

where \underline{R} is the internuclear vector, \underline{r} is the position vector of the electron, r_A and r_B are the distances between the electron and nuclei A and B respectively, and M_p is the mass of a proton.

- i. Explain what each of the 5 terms in this Hamiltonian represents. [3]
 - ii. Write down Schrödinger equations for electronic and nuclear motion in the Born-Oppenheimer approximation. [4]
 - iii. In writing the electronic Schrödinger equation in the Born-Oppenheimer approximation, which terms are neglected? [1]
- (c) Briefly outline the physical basis of the Franck-Condon principle and how it relates to the distribution of final vibrational states in transitions between molecular electronic states. Your answer should include an expression for the Franck-Condon factor in terms of the initial and final vibrational wavefunctions. [3]