SEMESTER 1 EXAMINATION 2014-2015

ATOMIC PHYSICS **MODEL ANSWERS**

Duration: 120 MINS (2 hours)

This paper contains 8 questions.

Answers to Section A and Section B must be in separate answer books

Answer **all** questions in **Section A** and **only two** questions in **Section B**.

Section A carries 1/3 of the total marks for the exam paper and you should aim to spend about 40 mins on it.

Section B carries 2/3 of the total marks for the exam paper and you should aim to spend about 80 mins on it.

An outline marking scheme is shown in brackets to the right of each question.

A Sheet of Physical Constants is provided with this examination paper.

Only university approved calculators may be used.

A foreign language translation dictionary (paper version) is permitted provided it contains no notes, additions or annotations.

Section A

A1. What are the physical observables associated with the principal quantum numbers n, l and m which are used to describe the electronic states of hydrogen? State the inequalities which limit the possible combinations of n, l and m. [5] **bookwork/seen** *Energy,* [1]

Orbital angular momentum squared [1]

and z component of the orbital angular momentum [1]

$l < n$, [1]

$-l \le m \le l$ [1]

A2. One of the electromagnetic emission lines for a hydrogen atom has wavelength 103 nm. Find out which series of emission lines this line belongs to and also find the initial principal quantum number n_i associated with the transition. The Rydberg energy can be assumed to be 13.6 eV. [5]

unseen $n_i = 3$ [1]

In fact **full marks** *if right number otherwise: Energies $E = -Ry/n^2$* [1]

$\Delta E = Ry\left(1/n_f^2 - 1/n_i^2\right)$ with $n_f = 1, 2,$ or 3. [1]

$\Delta E = hc/\lambda$ [0.5]

so $\Delta E = 12.04$ eV or $hc/(\lambda Ry) = 0.8851$ or $\lambda Ry/(hc) = 1.130$ [0.5]

so $1/n_i^2 = 1/n_f^2 - 0.8851 \Rightarrow n_f = 1$ so Lyman series [1]

and from there n_i.

A3. What is the Stark effect? Why can hydrogen atoms display a linear Stark effect and under what conditions? [6]

all bookwork/seen *The Stark effect is the shifting and splitting of spectral lines of atoms due to presence of an external static electric field.* [1]

The linear Stark effect is the name given to the case where these shifts are linear in the strength of the applied field. [1]

Quantum mechanically, the shift ΔEnergy for a hydrogen atom, is computed in perturbation theory from the matrix elements of $\mathbf{r} \cdot \mathbf{E}$. [1]

In the ground state of the hydrogen atom there is only one eigenstate Ψ_0 and

the wavefunction is spherically symmetric so $\langle \Psi_0 | \mathbf{r} \cdot \mathbf{E} | \Psi_0 \rangle$ vanishes, and no linear dependence is seen. *[1]*

If the hydrogen atom is in an excited state then there are several degenerate eigenstates Ψ_i with the same unperturbed energy. *[1]*

A linear Stark effect is then seen, as can be understood from diagonalising $\langle \Psi_i | \mathbf{r} \cdot \mathbf{E} | \Psi_j \rangle$ as follows from first order degenerate perturbation theory. *[1]*

A4. In terms of a general normalised wavefunction $\psi(x)$ and general Hamiltonian $\hat{H}$, give the integral which is the expectation value of the energy for a one dimensional system extending from negative to positive infinity in the x direction. If ψ_1, ψ_2 and ψ_3 are orthonormal eigenfunctions of the Hamiltonian with energies 2 eV, 3 eV and 12 eV respectively, compute the expectation value of the energy of the system when it is in the state described by the wavefunction

$$\psi = \frac{1}{7}(6\,\psi_1 + 3\,\psi_2 + 2\,\psi_3).\qquad [4]$$

Expectation value of the energy is **bookwork/seen**

$$\int_{-\infty}^{\infty} dx\,\psi^* \hat{H} \psi\,.$$

[1]

This is **unseen**

$$\mathrm{eV} \int_{-\infty}^{\infty} dx\,\frac{1}{49}(6\psi_1^* + 3\psi_2^* + 2\psi_3^*)(12\psi_1 + 9\psi_2 + 24\psi_3)\,,$$

using the eigenstate property and energy eigenvalues. Using orthornormality (NB integral expression not required but then the student needs to demonstrate in some other way that he/she understands that the eigenstate property and orthonormality are used, in order to get this mark) *[1]*

we thus have $\frac{1}{49}(72 + 27 + 48)$ eV *[1]*

which gives expectation value of energy $= 3$ eV. *[1]*

(Last three marks automatic if answer right, but in last mark give only 0.5 if units eV missing.)

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Section B

B1. (i) A Hamiltonian H_0 is represented by the matrix:

$$H_0 = \begin{pmatrix} 3 & 0 & -2 \\ 0 & \alpha & 0 \\ -2 & 0 & 3 \end{pmatrix} \text{ eV}\,,$$

where α is a dimensionless parameter. Show that $\frac{1}{\sqrt{2}}(1\ 0\ -1)$ is an eigenstate of the Hamiltonian and derive its eigenvalue. Find the other two eigenstates and the associated eigenenergies. [5]

unseen

$$\begin{pmatrix} 3 & 0 & -2 \\ 0 & \alpha & 0 \\ -2 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = 5 \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}\,,$$

so $\frac{1}{\sqrt{2}}(1\ 0\ -1)$ is an eigenstate with eigenenergy 5 eV *[1]*
By e.g. inspection, or standard brute force method, $(0\ 1\ 0)$ is an eigenstate
with eigenenergy α eV *[2]*
and by e.g. inspection or orthogonality, or again by standard brute force
method, $\frac{1}{\sqrt{2}}(1\ 0\ 1)$ is an eigenstate with eigenenergy 1 eV. *[2]*

(ii) A perturbation to the Hamiltonian is introduced:

$$H_p = \epsilon \begin{pmatrix} 0 & 1 & 0 \\ 1 & -1 & 2 \\ 0 & 2 & 3 \end{pmatrix} \text{ eV}\,,$$

where ϵ is a dimensionless small parameter. Setting $\alpha = \sqrt{3}$, use first order perturbation theory to compute approximately the eigenenergies of the new Hamiltonian $H = H_0 + H_p$. [4]

bookwork/seen *Use non-degenerate first order perturbation theory. Then the change in energy for eigenstate ψ is*

$$\Delta E = \langle \psi | H_p | \psi \rangle\,,$$ *[1]*

unseen *and thus eigenenergies at first order in ϵ are $(5 + 3\epsilon/2)$ eV,* [1]

$(\sqrt{3} - \epsilon)$ *eV* [1]

and $(1 + 3\epsilon/2)$ eV. [1]

(iii) For what values of α, would your method in (ii) be incorrect and why? [2]

  unseen *If two of the unperturbed energy levels are equal, so $\alpha = 1$ or 5 eV (half mark if just one given or the general reason given)* [1]

then there is degeneracy and one has to use degenerate perturbation theory corresponding to diagonalising H_p in this subspace (or any other reasonable explanation) [1]

(iv) Derive, using first order perturbation theory, formulae for the electron-electron energies for both the $S = 0$ and $S = 1$ excited states of helium in which one electron is in the $1s$ orbital and one electron is in a $2s$ orbital. Identify the direct and exchange components of the energies and give a physical interpretation of them. [9]

  bookwork/seen *We treat the electron-electron repulsion perturbatively using degenerate first order perturbation theory. Thus if $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is the unperturbed wavefunction, the perturbation to the energy is*

$$\Delta E = \langle \psi | \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} | \psi \rangle \,.$$ [1]

The correct unperturbed eigenstates to use are such that they have definite total spin S. Since the $S = 0(1)$ total spin state is odd (even) under exchange of the electrons, the spatial wavefunction must be even (odd) under exchange so that the overall state is odd under exchange of the two electrons [1]

as required by Pauli's exclusion principle (or because they are fermions). [1]

Thus (+ for $S = 0$ and − for $S = 1$):

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) \pm \psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1) \} \,,$$ [1]

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leading to $\Delta E = E_{direct} \pm E_{exchange}$, *where*   *[1]*

$$E_{direct} = \int \psi_{1s}^*(\mathbf{r}_1)\psi_{2s}^*(\mathbf{r}_2)\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2)\,dV_1 dV_2\,,$$ *[1]*

and

$$E_{exchange} = \int \psi_{1s}^*(\mathbf{r}_1)\psi_{2s}^*(\mathbf{r}_2)\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1)\,dV_1 dV_2\,.$$ *[1]*

The direct energy corresponds to the classical energy of the interaction i.e.
two charge densities which interact via the Coulomb interaction.   *[1]*
The exchange energy is a quantum mechanical effect associated with the
interference of the two electrons.   *[1]*

B2. (i) State what is meant physically by the Einstein coefficients A_{ij} and B_{ij}. [2]

bookwork/seen *B_{ij} is the* stimulated transition rate *(probability per unit time) for moving from state i to state j, per unit energy density of the electromagnetic field.* *[1]*

A_{ij} is the spontaneous transition rate *from state i to state j.* *[1]*

(ii) State all of the selection rules for an electric dipole optical transition for a multi-electron atom. [6]

bookwork/seen *$\Delta J = \pm 1, 0$ but not $J = 0 \to J = 0$* *[1]*

$\Delta M_J = \pm 1, 0$ *[1]*

$\Delta L = \pm 1, 0$ but not $L = 0 \to L = 0$ *[1]*

$\Delta S = 0$ *[1]*

For the electron undergoing the transition: $\Delta l = \pm 1$ *[1]*

Only one electron changes its configuration. *[1]*

(iii) Which of the following transitions are allowed and which forbidden? Where forbidden, state which selection rule or rules they break.

$$[Ar]\, 4s^2\, 3d^5\; {}^6S_{5/2} \quad \to \quad [Ar]\, 4s\, 3d^5\, 5p\; {}^6P_{5/2}$$
$$[Ne]\, 3s^2\, 3p^2\; {}^5D_0 \quad \to \quad [Ne]\, 3s\, 3p^2\, 3d\; {}^5P_0$$
$$[Ar]\, 3d^9\, 4s^2\, 4p^3\, 10d\; {}^4P_{3/2} \quad \to \quad [Ar]\, 3d^{10}\, 4s^2\, 4p^3\; {}^4S_{3/2}$$

[6]

unseen *Allowed.* *[1]*

Not allowed: $\Delta l = 2$ violating $\Delta l = \pm 1$, and $J = 0 \to J = 0$. *[3]*

Not allowed. Violates $\Delta l = \pm 1$. *[2]*

(iv) The dipole matrix element for the transition $[Ar]\, 4p_{1/2} \to [Ar]\, 3d_{3/2}$ in potassium, is measured to be $D \approx 7.98\, e\, a_0$, where a_0 is the Bohr radius. The wavelength of the emitted photon in this transition is $\lambda \approx 1.17\mu$m. Using Fermi's golden rule, and the relation between the Einstein A and B coefficients, estimate the spontaneous transition rate. [6]

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bookwork/seen *Fermi's golden rule gives us in the dipole approximation:*

$$B_{ij} = \frac{|\mathbf{D}_{ij} \cdot \mathbf{e}|^2}{2\varepsilon_0 \hbar^2} .$$

[2]

bookwork/seen *The spontaneous transition rate*

$$\frac{A_{ij}}{B_{ij}} = \frac{2h\nu^3}{c^3} .$$

[2]

unseen *Thus the spontaneous transition rate is*

$$A = \frac{(7.98)^2 e^2 a_0^2}{2\varepsilon_0 \hbar^2} \frac{2h}{\lambda^3} = \frac{2\pi(7.98)^2 e^2 a_0^2}{\varepsilon_0 \hbar \lambda^3} = 1.92 \times 10^7 \mathrm{s}^{-1} .$$

[2]

If the formula for the Bohr radius is recalled, then a simpler formula is:

$$A = \frac{2\pi(7.98)^2 a_0^2}{\varepsilon_0 \hbar \lambda^3} \frac{4\pi \hbar^2 \varepsilon_0}{m_e a_0} = \frac{4\pi (7.98)^2 h a_0}{m_e \lambda^3}$$

B3. (i) The z component of the angular momentum operator for a single particle is given by

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \, ,$$

in spherical polar coordinates. How is $\hat{L}_z$ related to symmetry under rotations around the z-axis? By deriving its eigenfunctions, explain how this leads to the existence of a conserved quantum number m for the hydrogen atom (in the approximation in which spin-orbit correction is neglected). [5]

bookwork/seen *$\hat{L}_z$ generates rotations around the z-axis /or/ it is conserved because the Hamiltonian is invariant under such rotations.* *[1]*
Eigenvalue equation is:

$$\hat{L}_z \Phi(\varphi) = \hbar m \, \Phi(\varphi) \, ,$$ *[1]*

so

$$\Phi(\varphi) = \exp im\varphi \, .$$ *[1]*

In order for Φ to be single valued, m must be an integer. *[1]*
The quantum number m is conserved for the electron in a hydrogen atom (when the spin-orbit correction is neglected) because the corresponding Hamiltonian is spatially rotationally invariant, the potential depending only the distance from the proton /or/ because $[\hat{L}_z, \hat{H}] = 0$. *[1]*

(ii) Describe the angular dependence of the probability distribution for the hydrogen states $[n = 2, l = 0, m = 0]$, $[n = 2, l = 1, m = 0]$, and $[n = 2, l = 1, m = -1]$. [3]

bookwork/seen *sphere,* *[1]*
dumbbell *[1]*
and donut (torus). *[1]*
NB. The student should demonstrate that the latter two have the z axis as the symmetry axis to get full marks. They can describe in words or draw appropriate pictures.

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(iii) How does the spin-orbit correction applied to hydrogen depend on orbital and spin angular momentum? What is the physical mechanism which gives rise to the spin-orbit correction? What effect does the spin-orbit correction have on the quantum numbers used to label the states of hydrogen?   [8]

bookwork/seen *The spin-orbit correction is proportional to $\mathbf{l} \cdot \mathbf{s}$.*   *[1]*

In the rest frame of the nucleus it produces an electric field. In the rest frame of the electron this electric field is transformed into a magnetic field.   *[1]*

The magnitude of the magnetic field is proportional to the rate at which the electron orbits and thus the orbital angular momentum.   *[1]*

The electron has a magnetic moment which is proportional to its spin.   *[1]*

A magnetic moment in the presence of a magnetic field has an energy given by $-\mathbf{m} \cdot \mathbf{B}$.   *[1]*

Thus the electron in a hydrogen atom has a component of energy proportional to $\mathbf{l} \cdot \mathbf{s}$. The effect of the spin orbit correction is that m_l and m_s are no longer good quantum numbers   *[1]*

and are replaced by j and m_j   *[1]*

which are associated with the total angular momentum squared and the z component of the total angular momentum.   *[1]*

(iv) The sum of the relativistic fine structure corrections for hydrogen is given by

$$\Delta E = -\frac{\alpha^2}{n^2} \left[\frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right] E_n^0 .$$

How many distinct spectral lines due to this fine structure are seen for optical transitions between the $n = 3$ and $n = 2$ levels? Give your reasoning.   [4]

unseen *The $n = 3$ level can have $l = 2, 1, 0$ and thus $j = 5/2, 3/2, 1/2$.*   *[1]*

The $n = 2$ level can have $l = 1, 0$ and thus $j = 3/2, 1/2$.   *[1]*

The optical selection rules allow $\Delta j = 0, \pm 1$. Therefore there are the following allowed transitions: $5/2 \to 3/2; 3/2 \to 3/2, 1/2; 1/2 \to 3/2, 1/2;$

which makes 5 in all. *[1]*

The energy corrections for all these transitions are different *[1]*

so there are 5 lines in the spectrum.

B4. (i) Describe what is meant by quantum defect as applied to alkali metal atoms and the physical mechanism which leads to the quantum defects.   [4]

bookwork/seen *Quantum defect refers to the fact that in the alkali metals the energy levels of the **outer most electron** are **almost that of the hydrogen** atom*   *[1]*
*except for the fact that the principal quantum number in the expression for the energy states in hydrogen is replaced by the **principal quantum number minus the so called quantum defect** for the alkali metals.*   *[1]*
*The quantum defect comes about because, whilst in general the outer most electron is outside all of the other electrons and therefore **the inner electrons screen***   *[1]*
*the nuclear charge, depending on its orbital angular momentum it does spend some time **inside** at least some of the other electrons and thus **experiences a more negative** potential than it would if it was in a hydrogen atom **leading to its energy being decreased**.*   *[1]*

(ii) What is the maximum number of electrons that an s orbital can hold, and why? For the p and d orbitals respectively, what is the maximum number of electrons that they can hold, and why? Why does the fourth row of the periodic table have 18 atoms in it whilst the third row has only 8?   [6]

bookwork/seen *The maximum number of electrons that the s, p and d orbitals can hold is 2, 6 and 10 respectively.*   *[1.5]*
This is so because there are respectively 1, 3 and 5 orbitals corresponding to $l = 0, 1, 2$ and multiplicity $2l + 1$ *[0.5]*
and spin up and spin down for the electron   *[0.5]*
and furthermore by Pauli's exclusion principle there can be no two electrons with the same quantum numbers.   *[0.5]*
The third row only fills the $3s$ and $3p$ orbitals – adding up to 8 atoms.   *[1]*
In the fourth row the first additional electrons go into the $4s$ orbital as the quantum defect associated with the $4s$ orbital means it is lower in energy

than the $3d$ *orbital.*   *[1]*

The next ten electrons go into the $3d$ *orbital and the next 6 go into the* $4p$
orbital.   *[1]*

(iii) Name the two perturbations usually applied to the central field Hamiltoni-
ans to obtain the first layer of fine structure for multi-electron atoms. Which
is more important for small atomic number atoms?   [3]

bookwork/**seen** *The non-central potential*   *[1]*
and the spin-orbit correction.   *[1]*
The non-central potential is more important for small atomic number atoms.

[1]

(iv) Assume that LS coupling is a good approximation in the atoms listed
below. For each of the electron configurations state whether Hund's
rules can be used. If so, predict the ground state and write down the
corresponding Term Symbol.

(a) $Fe = [Ar]\, 3d^6\, 4s^2$

(b) $Si = [Ne]\, 3s^2\, 3p^2$

(c) $Mn = [Ar]\, 3d^5\, 4s^2$

(d) $Nb = [Kr]\, 4d^4\, 5s^1$ [7]

unseen *mark given if not stated that Hund's rules apply but correctly*
assumed.

(a) yes $^5D_4$ *($\uparrow\downarrow,\uparrow,\uparrow,\uparrow,\uparrow$)*   *[2]*
(b) yes $^3P_0$ *($\uparrow,\uparrow,$)*   *[2]*
(c) yes $^6S_{5/2}$ *($\uparrow,\uparrow,\uparrow,\uparrow,\uparrow$)*   *[2]*
(d) no (2 shells unfilled)   *[1]*

END OF PAPER