SEMESTER 1 EXAMINATION 2017-2018

ATOMIC PHYSICS **MODEL ANSWERS**

Duration: 120 MINS (2 hours)

This paper contains 9 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 is required in quantum mechanics for a quantity to be conserved? Show that this implies that for the linear momentum of an electron to be conserved in the presence of a potential, the potential must be uniform. [4]

all bookwork/seen For a quantity to be conserved the operator associated with its observable must commute with the Hamiltonian of the system.

[1]

The operator associated with linear momentum is

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x},$$

and this will have to commute with the Hamiltonian. It commutes with the kinetic term $\hat{p}^2/2m$ since derivatives commute.

[1]

In order for it to commute with the potential energy part of the Hamiltonian, $V(\mathbf{r})$, we have to have, for all wavefunctions $\psi(\mathbf{r})$,

$$\frac{\partial}{\partial x}(V\psi) - V\frac{\partial}{\partial x}(\psi) = \frac{\partial V}{\partial x}\psi + V\frac{\partial \psi}{\partial x} - V\frac{\partial \psi}{\partial x} = \frac{\partial V}{\partial x}\psi = 0$$
 [1]

at all points in space i.e. that $\frac{\partial}{\partial x}V(\mathbf{r})=0$ everywhere. Thus the potential is uniform throughout space.

[1]

- A2. One of the electromagnetic emission lines for a hydrogen atom has wavelength 410.2 nm. Assuming that the Rydberg energy is 13.605 eV:
 - (a) Find out which series of emission lines this line belongs to.
 - (b) Find the initial principal quantum number n_i associated with the transition.

[5]

unseen

Energies
$$E = -Ry/n^2$$
 [1]

$$\Delta E = Ry (1/n_f^2 - 1/n_i^2)$$
 [1]

$$\Delta E = hc/\lambda \tag{0.5}$$

so
$$\Delta E = 3.015 \text{ eV or } hc/(\lambda Ry) = 0.222 \text{ or } \lambda Ry/(hc) = 4.511$$
 [0.5]

so
$$1/n_i^2 = 1/n_f^2 - 0.222$$
 that is $n_f = 2$ as we need $n_i > n_f$. So Balmer series [1] and from there $n_i = 6$.

- **A3.** (a) 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. [1]
 - (b) If $\psi_1(x)$, $\psi_2(x)$ and $\psi_3(x)$ are orthonormal eigenfunctions of the Hamiltonian with energies 2 eV, 6 eV and 5 eV respectively, compute the expectation value of the energy of the system when it is in the state described by the wavefunction

$$\psi(x) = \frac{1}{\sqrt{26}} \left[3 \psi_1(x) + \psi_2(x) + 4 \psi_3(x) \right].$$

[3]

bookwork/seen

$$\int_{-\infty}^{\infty} dx \, \bar{\psi}(x) \hat{H} \psi(x) \,. \tag{1}$$

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$$\text{eV} \int_{-\infty}^{\infty} \!\! dx \, \frac{1}{26} (3\bar{\psi}_1 + \bar{\psi}_2 + 4\bar{\psi}_3) (6\psi_1 + 6\psi_2 + 20\psi_3) \,,$$

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)

we thus have $\frac{1}{26}(18+6+80) \text{ eV}$ [1]

which gives expectation value of energy = 4 eV. [1]

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

[1]

A4. What is the expansion theorem in quantum mechanics and what properties of the eigenstates of a Hermitian operator are usually used to calculate any particular expansion? [3]

bookwork/seen

That a general state of the system can be represented by a unique linear combination of the eigenstates of any Hermitian operator calculated with the same boundary conditions as the general state.

[2]

Orthonormality or Orthogonality.

[1]

A5. Consider two electrons, one in a p orbital and one in a d orbital. What is the maximal projection along an axis of the total angular momentum of the two electrons (including the spins)? [4]

bookwork/seen

The first electron has L=1 and $S=\frac{1}{2}$, so $J_1=L+S=\frac{1}{2}$ or $\frac{3}{2}$

The second electron has L=2 and $S=\frac{1}{2}$, so $J_2=L+S=\frac{3}{2}$ or $\frac{5}{2}$

The total angular momentum $J = J_1 + J_2$ takes thus values between 0 and 4, with 4 being the maximum

[2]

Section B

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

$$H_0 = \begin{pmatrix} 1 & 0 & 2 \\ 0 & \alpha & 0 \\ 2 & 0 & 4 \end{pmatrix} \text{ eV},$$

where α is a dimensionless parameter.

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

[5]

unseen

$$\begin{pmatrix} 1 & 0 & 2 \\ 0 & \alpha & 0 \\ 2 & 0 & 4 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 2 \end{pmatrix} = 5 \begin{pmatrix} 1 \\ 0 \\ 2 \end{pmatrix},$$

so $\frac{1}{\sqrt{5}}(1\ 0\ 2)$ 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

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

For the last two questions one point is given for the eigenvalue and one for the eigenvector.

(ii) A perturbation is introduced to the Hamiltonian:

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

where ϵ is a dimensionless small parameter. Setting $\alpha = 1$, use first

[2]

[2]

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

$$\Delta E = \langle \psi | H_p | \psi \rangle \,, \tag{1}$$

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and thus eigenenergies at first order in ϵ are

$$(5 - 4\epsilon/5) \text{ eV}$$

$$(1 - \epsilon) \text{ eV}$$

$$9\epsilon/5 \text{ eV}$$

$$[1]$$

(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 $\alpha=0$ or 5 (half mark if just one given or the general reason given). Full mark wether eV is used or not [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) (a) Derive, using first order perturbation theory, formulae for the electron-electron Coulomb 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.
 - (b) Identify the direct and exchange components of the energies and give physical interpretations of them.

[9]

[1]

[1]

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

as required by Pauli's exclusion principle (or because they are fermions). [1] Thus (+ for S = 0 and - for S = 1):

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

leading to $\Delta E = E_{direct} \pm E_{exchange}$, where

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

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.

B2. (i) The Hamiltonian for a single electron in the presence of a nucleus with atomic number *Z* is

$$\hat{H}_0 = \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \right] .$$

Show that the eigenstates $\psi^Z_{nlm}(\mathbf{r})$ and eigenvalues E^Z_{nlm} of this problem are those for the hydrogen atom $\psi^H_{nlm}(\mathbf{r})$ and E^H_{nlm} scaled in the following ways:

$$\psi_{nlm}^{Z}(\mathbf{r}) = Z^{3/2}\psi_{nlm}^{H}(Z\mathbf{r}), \qquad E_{nlm}^{Z} = Z^{2}E_{nlm}^{H}.$$

[5]

bookwork/seen

Replace the spatial co-ordinate with the new one r' = Zr [1]

The kinetic term due to the derivative becomes $Z^2 \frac{\partial^2}{\partial x_i^2}$ [1]

The potential energy becomes $-\frac{Z^2e^2}{4\pi\epsilon_0 r'}$ [0.5]

The Schroedinger equation has thus the same form of the one for the hydrogen atom by rescaling the energy and the wavefunctions [1]

Normalising we have

$$\int dV |\psi^{Z}(\mathbf{r})|^{2} = Z^{3} \int dV |\psi^{H}(Z\mathbf{r})|^{2}$$

[0.5]

[1]

and from r' = Zr we have $dV' = Z^3 dV$ and thus

$$\int dV |\psi^{Z}(\mathbf{r})|^{2} = \int dV' |\psi^{H}(\mathbf{r}')|^{2} = 1$$
 [1]

(ii) Why are the first ionisation energies of a Helium atom with one excited electron very similar to the corresponding ionisation energies of a Hydrogen atom? [3]

bookwork/seen

The excited electron spends nearly all of its time outside the unexcited electron wavefunction.

A spherical Gaussian surface through the position of the excited electron will therefore have a net charge of +1e inside it. [1]

Therefore the electric potential/field experienced by the excited electron is almost identical to that of an electron orbiting a +1e hydrogen nucleus and will have the same energy levels. [1]

(iii) The energy levels for the outer electron in an alkali metal atom are well approximated by

$$E_n = (-Ry)/(n - \delta_l)^2,$$

where Ry is the Rydberg energy and δ_l is the quantum defect. What is the physical reason for the quantum defect? How does the quantum defect vary with angular momentum and why? [4]

bookwork/seen

The outer electron in an alkali metal atom spends most of its time outside of the other electrons in the atom and thus as in part (i) experiences a potential close to that of the hydrogen nucleus.

[1] However, particularly for small angular momentum states it spends some fraction of its time inside the screening electrons and so its energy levels are actually lower in energy than for the hydrogen nucleus. This is physical reason for the quantum defect

[1] The quantum defect decreases with increasing angular momentum

[1] because high angular momentum states have a smaller probability of the outer electron being found inside the other electrons because of the centrifugal energy term.

[1]

(iv) A Helium atom is in an excited state with one electron in the 1s state, represented by the wavefunction $\psi_{1s}(r)$, and one electron in the 3p state, represented by the wavefunction $\psi_{3p}(r)$. Each electron can be either spin up or spin down represented by $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively. What are the

four possible two particle states in which the atom can be? [4]

bookwork/seen

$$\frac{1}{2} \left(\psi_{3p}(r_1) \psi_{1s}(r_2) + \psi_{3p}(r_2) \psi_{1s}(r_1) \right) (|\downarrow\rangle| \uparrow\rangle - |\uparrow\rangle| \downarrow\rangle)$$

$$[1]$$

$$\frac{1}{2} \left(\psi_{3p}(r_1) \psi_{1s}(r_2) - \psi_{3p}(r_2) \psi_{1s}(r_1) \right) (|\downarrow\rangle| \uparrow\rangle + |\uparrow\rangle| \downarrow\rangle)$$

$$[1]$$

 $\frac{1}{\sqrt{2}} \left(\psi_{3p}(r_1) \psi_{1s}(r_2) - \psi_{3p}(r_2) \psi_{1s}(r_1) \right) |\uparrow\rangle |\uparrow\rangle$

[1]

$$\frac{1}{\sqrt{2}} \left(\psi_{3p}(r_1) \psi_{1s}(r_2) - \psi_{3p}(r_2) \psi_{1s}(r_1) \right) |\downarrow\rangle |\downarrow\rangle$$

[1]

(v) For each of the four two particles states written down in part (iv), calculate by how many dipole-allowed transitions the state can decay into a lower energy state. Give your reasoning. [4]

unseen

(iv) are correct.

[1]

[1]

[1]

[1]

B3. (i) 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? [4]

bookwork/seen The spin-orbit correction is proportional to $l \cdot s$.

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

The electron has a magnetic moment which is proportional to \mathbf{s} . A magnetic moment in the presence of a magnetic field has an energy given by $-\mathbf{m} \cdot \mathbf{B}$. 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 and are replaced by j and m_j which are associated with the total angular momentum squared and the z component of the total angular momentum.

- (ii) (a) What is the maximum number of electrons that an *s* orbital can hold, and why?
 - (b) For the p and d orbitals respectively, what are the maximum numbers of electrons that they can hold, and why?
 - (c) 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

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) Write the three Hund's rules. [3]

bookwork/seen

- 1) The maximum multiplicity state (maximum S) is the lowest in energy [1] 2) The maximum orbital momentum state (maximum L) is the lowest in energy [1] 3) For less than half-filled orbitals the total angular momentum with the lowest energy is the minimum one |L-S|, otherwise it is the maximum one |L+S|
- (iv) Assume that *LS* coupling is a good approximation in the atoms listed below. For each of the electron configurations listed below 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) $C = 1s^2 2s^2 2p^2$,
 - (c) Nb = [Kr] $4d^4 5s^1$,
 - (d) Mn = [Ar] $3d^5 4s^2$. [7]

unseen

Mark given if not stated that Hund's rules apply but correctly assumed. Mark also given if only the correct term symbol is given.

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

B4. (i) State all of the selection rules for an electric dipole optical transition for a multi-electron atom. [4]

bookwork/seen

$$\Delta J = \pm 1, 0$$
 but not $J = 0 \rightarrow J = 0$

$$\Delta M_J = \pm 1, 0$$

$$\Delta L = \pm 1, 0$$
 but not $L = 0 \rightarrow L = 0$

$$\Delta S = 0$$

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

Only one electron changes its configuration.

Three rules correct: 1 point. Four correct: 2 points. Five correct: 3 points. All correct: 4 points.

(ii) Consider the following transitions of the Na atom:

(a)
$$4d^2D_{3/2} \rightarrow 3p^2P_{1/2}$$
,

(b)
$$3p^2P_{3/2} \rightarrow 3s^2S_{1/2}$$
,

(c)
$$3p^2P_{3/2} \rightarrow 3p^2P_{1/2}$$
,

(d)
$$3p^2P_{1/2} \rightarrow 3s^2S_{1/2}$$
.

(e)
$$4d^2D_{5/2} \rightarrow 3p^2P_{1/2}$$
,

$$(f) \quad 4d^2D_{3/2} \ \to \ 3p^{1}P_{3/2}.$$

Which are allowed and which forbidden? For those which are forbidden, state which selection rule or rules they break. [6]

unseen

(a) Allowed	[1]
(b) Allowed	[1]
(c) Forbidden, $\Delta l = 0$	[1]
(d) Allowed	[1]
(e) Forbidden, $\Delta J = 2$	[1]
(f) Forbidden, $\Delta S \neq 0$	[1]

(iii) What does Fermi's golden rule predict for optical transitions and what is the

[1]

formula for that prediction? Clearly identify all the terms in this equation. [4]

bookwork/seen

Fermi's golden rule predicts the rate of photon absorption by an atomic transition

$$\frac{|\mathbf{D}_{nj}\cdot\mathbf{e}|^2}{9\hbar^2}\rho(\nu)$$
 [1]

where
$$\mathbf{D}_{ni} = \int \psi_n(r) [-e\mathbf{r}] \psi_i(r) dV$$
 [1]

and
$$\rho(v)$$
 is the energy density of the electromagnetic field [1]

(iv) We can write the wavefunctions of the hydrogen atom with quantum number n, l, m as $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m}(\theta,\phi)$. Given

$$R_{1,0}(r) = 2a_0^{-\frac{3}{2}} \exp(-r/a_0),$$

$$R_{2,1}(r) = \frac{1}{\sqrt{3}} (2a_0)^{-\frac{3}{2}} (r/a_0) \exp(-r/2a_0),$$

$$Y_{0,0}(\theta, \phi) = \sqrt{\frac{1}{4\pi}},$$

$$Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta,$$

and the integral

$$\int_0^\infty x^4 e^{-x} dx = 24,$$

calculate all the three Cartesian components of the vector dipole matrix element $\mathbf{D} = e\mathbf{r}$ between the states $\psi_{2,1,0}(r,\theta,\phi)$ and $\psi_{1,0,0}(r,\theta,\phi)$. [6]

bookwork/seen

$$\begin{split} D_x &= \int_0^\infty r^2 dr R_{1,0} R_{2,1} \int_0^\pi d\theta \int_0^{2\pi} d\phi \, [er \sin\theta \cos\phi] Y_{0,0} Y_{1,0} \\ D_y &= \int_0^\infty r^2 dr R_{1,0} R_{2,1} \int_0^\pi d\theta \int_0^{2\pi} d\phi \, [er \sin\theta \sin\phi] Y_{0,0} Y_{1,0} \\ D_z &= \int_0^\infty r^2 dr R_{1,0} R_{2,1} \int_0^\pi d\theta \int_0^{2\pi} d\phi \, [er \cos\theta] Y_{0,0}(\theta,\phi) Y_{1,0}(\theta,\phi) \end{split}$$

Only one correct: 1 point. The three correct: 2 points.

unseen

The third, doing the angular integral becomes $\frac{1}{3\sqrt{2}a^4}\int_0^\infty \exp(-3r/2a_0)r^4dr$ [1] and substituting the value of the integral $D_z=\frac{128\sqrt{2}ea_0}{243}$ [1]

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