

Imperial College London

BSc/MSci EXAMINATION June 2012

This paper is also taken for the relevant Examination for the Associateship

ELECTRONS IN SOLIDS AND APPLICATIONS OF QUANTUM MECHANICS

For 2nd-Year Physics Students

Wednesday, 13th June 2012: 10:00 to 12:00

*Answer ALL parts of Section A, plus
ONE question from Section B and ONE question from Section C.*

Formula sheets relevant to questions 2, 5 and 6 (AppQM) are given separately.

Marks shown on this paper are indicative of those the Examiners anticipate assigning.

General Instructions

Complete the front cover of each of the FOUR answer books provided.

If an electronic calculator is used, write its serial number at the top of the front cover of each answer book.

USE ONE ANSWER BOOK FOR EACH QUESTION.

Enter the number of each question attempted in the box on the front cover of its corresponding answer book.

Hand in FOUR answer books even if they have not all been used.

You are reminded that Examiners attach great importance to legibility, accuracy and clarity of expression.

Useful Formulae

Harmonic oscillator

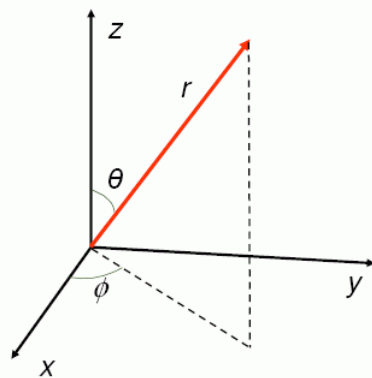
$$u_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}, \quad E_0 = \frac{1}{2}\hbar\omega$$

$$u_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-m\omega x^2/2\hbar}, \quad E_1 = \frac{3}{2}\hbar\omega$$

$$u_2 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}} \left(\frac{2m\omega}{\hbar} x^2 - 1\right) e^{-m\omega x^2/2\hbar}, \quad E_2 = \frac{5}{2}\hbar\omega$$

$$u_3 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{m\omega}{3\hbar}} x \left(\frac{2m\omega}{\hbar} x^2 - 3\right) e^{-m\omega x^2/2\hbar}, \quad E_3 = \frac{7}{2}\hbar\omega$$

Spherical coordinates



$$r = |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\nabla_{sph} = \frac{\partial}{\partial r} \hat{r} + \frac{\partial}{\partial \theta} \frac{\hat{\theta}}{r} + \frac{\partial}{\partial \phi} \frac{\hat{\phi}}{r \sin \theta}$$

$$\nabla_{sph}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\int d^3r f(\mathbf{r}) = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi f(r, \theta, \phi)$$

Angular momentum

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

Component commutation relation

$$i\hbar \hat{L} = \hat{L} \times \hat{L}$$

Hydrogenic atom

Energies

$$E_n = -\frac{E_h}{2} \frac{Z^2}{n^2}, \quad E_h = \frac{\hbar^2}{m_e a_0^2} = 27.2 \text{ eV}$$

Wavefunctions

$$\psi_{nlm}(\mathbf{r}, t) = u_{nlm}(\mathbf{r}) e^{-iE_n t / \hbar}$$

$$u_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

Radial equation

$$\hat{H}\chi = E\chi$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V'(r)$$

$$V'(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + l(l+1) \frac{\hbar^2}{2mr^2}$$

$$\chi = \chi_{nl}(r) = rR_{nl}$$

Radial functions

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-(Zr/a_0)}$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-(Zr/2a_0)}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) e^{-(Zr/2a_0)}$$

$$R_{30}(r) = 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2 r^2}{27a_0^2} \right) e^{-(Zr/3a_0)}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{Zr}{6a_0} \right) \left(\frac{Zr}{a_0} \right) e^{-(Zr/3a_0)}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right)^2 e^{-(Zr/3a_0)}$$

Spherical harmonics

$$Y_{00} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{2\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$$Y_{2\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

Parity

$$Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l Y_{lm}(\theta, \varphi)$$

Photon wavelength and energy

$$\lambda E = 1240 \text{ nm} \cdot \text{eV}$$

Atomic units

Physical quantity	Name of unit	Symbol for unit	Value of unit in SI
mass	electron rest mass	m_e	$9.109\,3897(54) \times 10^{-31} \text{ kg}$
charge	elementary charge	e	$1.602\,177\,33(49) \times 10^{-19} \text{ C}$
action	Planck constant/ 2π ¹	\hbar	$1.054\,572\,66(63) \times 10^{-34} \text{ J s}$
length	bohr ¹	a_0	$5.291\,772\,49(24) \times 10^{-11} \text{ m}$
energy	hartree ¹	E_h	$4.359\,7482(26) \times 10^{-18} \text{ J}$
time		\hbar/E_h	$2.418\,884\,3341(29) \times 10^{-17} \text{ s}$
velocity ²		$a_0 E_h / \hbar$	$2.187\,691\,42(10) \times 10^6 \text{ m s}^{-1}$
force		E_h / a_0	$8.238\,7295(25) \times 10^{-8} \text{ N}$
momentum, linear		\hbar / a_0	$1.992\,8534(12) \times 10^{-24} \text{ N s}$
electric current		$e E_h / \hbar$	$6.623\,6211(20) \times 10^{-3} \text{ A}$
electric field		$E_h / e a_0$	$5.142\,2082(15) \times 10^{11} \text{ V m}^{-1}$
electric dipole moment		$e a_0$	$8.478\,3579(26) \times 10^{-30} \text{ C m}$
magnetic flux density		$\hbar / e a_0^2$	$2.350\,518\,08(71) \times 10^5 \text{ T}$
magnetic dipole moment ³		$e \hbar / m_e$	$1.854\,803\,08(62) \times 10^{-23} \text{ J T}^{-1}$

(1) $\hbar = h/2\pi$; $a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$; $E_h = \hbar^2 / m_e a_0^2$.

(2) The numerical value of the speed of light, when expressed in atomic units, is equal to the reciprocal of the fine structure constant α ; $c/(\text{au of velocity}) = \hbar / a_0 E_h = \alpha^{-1} \approx 137.035\,9895(61)$.

(3) The atomic unit of magnetic dipole moment is twice the Bohr magneton, μ_B .

$$m_e = \frac{\hbar^2}{E_h a_0^2} \quad E_h = \frac{e^2}{4\pi\epsilon_0 a_0}$$

Electric field amplitude vs. intensity in an EM wave

$$F = \sqrt{\frac{8\pi}{c4\pi\epsilon_0}} \sqrt{I} \quad (\text{SI})$$

$$F = \sqrt{8\pi/c} \sqrt{I} \quad (\text{atomic units})$$

$$1 \text{ a.u. intensity} = \frac{E_h^2}{a_0^2 \hbar} = 6.436 \times 10^{15} \text{ W/cm}^2$$

$$\equiv 22.02 \times 10^{10} \text{ V/m} = 0.4283 E_h / (e a_0)$$

$$F / \frac{\text{V}}{\text{cm}} = 27.48 \sqrt{I / \frac{\text{W}}{\text{cm}^2}}$$

$$F / \frac{E_h}{e a_0} = 5.338 \times 10^{-9} \sqrt{I / \frac{\text{W}}{\text{cm}^2}}$$

Dirac notation

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$$

$$\langle \phi | \psi \rangle = \int \phi^*(\mathbf{r}) \psi(\mathbf{r}) d^3r$$

$$\langle \phi | \hat{Q} | \psi \rangle = \int \phi^*(\mathbf{r}) \hat{Q} \psi(\mathbf{r}) d^3r$$

$$\langle \phi | \hat{Q} | \psi \rangle^* = \langle \psi | \hat{Q}^\dagger | \phi \rangle$$

$$\hat{\mathbf{r}} | \mathbf{r} \rangle = \mathbf{r} | \mathbf{r} \rangle$$

$$Y_{lm}(\theta, \varphi) = \langle \theta \varphi | l m \rangle$$

$$u_{nlm}(\mathbf{r}) = \langle \mathbf{r} | n l m \rangle$$

$$u_i(\mathbf{r}) = \langle \mathbf{r} | i \rangle$$

$$\langle i | j \rangle = \delta_{ij} \quad \langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$$

$$\sum_i |i\rangle \langle i| = \hat{1} \quad \int d^3r | \mathbf{r} \rangle \langle \mathbf{r} | = \hat{1}$$

Interaction with electromagnetic radiation

$$\mathbf{F} = \epsilon F_0 \cos(\omega t)$$

$$\mu = -e \langle 2 | \boldsymbol{\epsilon} \cdot \mathbf{r} | 1 \rangle$$

$$\Omega = -\frac{\mu F_0}{2\hbar}$$

$$I = \frac{c\epsilon_0}{2} F_0^2$$

$$I_{\text{indoor}} \approx 1 \text{ W/m}^2$$

$$I_{\text{sunlight}} \approx 1 \text{ kW/m}^2$$

$$T_{\text{Sun surface}} \approx 5800 \text{ K}$$

$$A_{21} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{21}$$

$$B_{12} = \frac{\pi \mu^2}{\epsilon_0 \hbar^2}$$

$$I(\omega) = c \rho(\omega)$$

$$\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / kT} - 1}$$

Spin

$$\hat{S} = \frac{\hbar}{2} \boldsymbol{\sigma} \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Helium-like systems**Ionisation and detachment energies****Coulomb integral for the ground state**

$$J = \langle 1s | \langle 1s | \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} | 1s \rangle | 1s \rangle = \frac{5}{8} E_h Z$$

Pilot wave theory

$$\psi = R e^{iS/\hbar}$$

$$\mathbf{v} = \frac{\nabla S}{m}$$

$$Q = -\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R}$$

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

Mathematics

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^{\infty} x^4 e^{-x^2} dx = \frac{3\sqrt{\pi}}{4}$$

Dirac delta

$$\int d^3 r' f(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') = f(\mathbf{r})$$

$$\delta(-\mathbf{r}) = \delta(\mathbf{r})$$

2 May 2012

SECTION A (Compulsory)

1.

(i) What is a hole? How does its charge, effective mass, and wavevector differ from that of an electron in the same band?

[3 marks]

(ii) The energy E of quantum state n for a 1-dimensional particle-in-a-box is given by:

$$E = \frac{h^2 n^2}{8mL^2}$$

where m is the mass of an electron and L is the length of the box. Find the lowest energy transition ΔE_p of a system of non-interacting electrons of number $2p$, where p is an integer variable. Show that for a nano-scale solid of size $L = pd$, where d is the shortest sub-unit containing 2 electrons, that ΔE_p is proportional to $1/p$ (for large p).

[3 marks]

(iii) Using sketches in k -space, briefly describe how electrical conduction occurs in the 3-dimensional free electron model.

[3 marks]

(iv) The electron n and hole p concentration in a semiconductor are given by:

$$n = N_C \exp(-(E_C - E_F)/k_B T)$$

$$p = N_V \exp(-(E_F - E_V)/k_B T)$$

where N_C and N_V are the effective density of states for the conduction and valence bands, respectively, E_C and E_V are the energies at the conduction and valence band edges, respectively, E_F is the Fermi level energy and T is temperature. Using these equations, find the relationship between the intrinsic carrier density n_i and the energy gap E_G of the semiconductor.

[3 marks]

[Total 12 marks]

2. In a vacuum ultraviolet (VUV) helium lamp a helium atom is ionised at time $t = 0$ and its remaining electron is left in the following superposition of states:

$$|\psi_0\rangle = A(2 |1\ 0\ 0\rangle - (1 + i) |2\ 1\ 0\rangle),$$

where A is a real positive normalisation constant and $|n\ l\ m\rangle$ the eigenvectors corresponding to the energy eigenfunctions $u_{nlm}(\mathbf{r})$.

- (i) Calculate the normalisation constant A . [1 mark]
- (ii) Calculate in atomic units the energies of the two states making up the $|\psi_0\rangle$ superposition. [2 marks]

After the ionisation at $t = 0$, state $|\psi_0\rangle$ starts to evolve in time becoming a new state $|\psi(t)\rangle$.

- (iii) Write down the expression for $|\psi(t)\rangle$ in terms of the energies you found in part (ii), assuming there is no emission of radiation. [1 mark]
- (iv) If, however, the state were to emit radiation:
 - (a) Calculate the wavelength of this radiation in SI units. [1 mark]
 - (b) Find the polarization of this radiation and justify your answer. [1 mark]
- (v) At time $t = 15$ fs a measurement of the orbital angular momentum squared is performed on state $|\psi(t)\rangle$ and a result of $2\hbar^2$ is found.
 - (a) Write down the state $|\psi'\rangle$ of vector $|\psi(t)\rangle$ immediately after the measurement. Use the correct normalisation constant assuming it is real positive and justify your answer. [1 mark]
 - (b) Is state $|\psi'\rangle$ an eigenstate of the parity operator? Justify your answer. [1 mark]

[Total 8 marks]

SECTION B

3.

(i) Consider the 1-dimensional free electron model (1D FEM) for a macroscopic solid of length L .

(a) What are the Born von Karman boundary conditions, and why are they used?

[2 marks]

(b) Write down the time independent Schrödinger equation for the solid, and show that it has a solution of the form:

$$\psi(x) = \frac{1}{\sqrt{L}} \exp(ik_x x)$$

for electron wavevector k_x values.

[4 marks]

(ii) Next consider the 3-dimensional free electron model (3D FEM) for a cube shaped solid of volume $V = L^3$ containing N electrons.

(a) Using the volume in k -space occupied by each allowed state in the 3D FEM, show that the Fermi wavevector is:

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

and find the Fermi energy E_F .

[3 marks]

(b) Show that in the 3D FEM the density of states is:

$$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

[3 marks]

(iii) (a) By considering the number of thermally excited electrons at the Fermi energy E_F at temperature T , show that the total thermal energy of these excited electrons is:

$$\Delta U = D(E_F) (k_B T)^2$$

[2 marks]

(b) Using the answers to part (ii), show that the heat capacity C_V of the solid is given by:

$$C_V = \frac{3}{2} N k_B \left(\frac{2k_B T}{E_F} \right)$$

[4 marks]

(c) Assume that the crystal structure is simple cubic, the length of the unit cell a is 0.35 nm, there is one atom of valency 2 per unit cell and $T = 30$ K. Calculate the ratio of the 3D FEM value of C_V to the classical value of C_V .

[2 marks]

[Total 20 marks]

4. (i) A 1-dimensional solid has a periodic potential of the form:

$$V(x) = V(x + na)$$

where n is an integer and a is the lattice repeat unit. Bloch electrons in this solid have wavefunctions of the form:

$$\psi(x) = u_k(x) \exp(ik_x x)$$

where:

$$u_k(x) = u_k(x + na)$$

- (a) Show that the plane wave part of the Bloch wavefunction shifts its phase angle by $k_x na$ between neighbouring unit cells.

[3 marks]

- (b) Show that there is an equal probability of finding the Bloch electron in every unit cell.

[4 marks]

- (ii) The Kronig-Penney model for Bloch electrons in this periodic potential results in a solution of the form:

$$\cos k_x a = \left(\cos qa + \frac{ma}{\hbar^2} U_0 \frac{\sin qa}{qa} \right)$$

where symbols have their usual meaning.

- (a) Sketch the variation of the terms in the brackets with qa . Indicate the values where solutions of the equation are valid.

[3 marks]

- (b) In the limit of small k_x and small U_0 , show that the Kronig-Penney model solution can be rewritten as:

$$E = \frac{\hbar^2}{2ma^2} \frac{6U_1}{U_1 + 3} + \frac{\hbar^2 k_x^2}{2m} \frac{3}{U_1 + 3}$$

where $U_1 = maU_0/\hbar^2$ [Note: upon using the trigonometric expansions, you must include the first two terms].

[5 marks]

- (c) Sketch the E vs k_x dispersion relationship for the Kronig-Penney model for large and small U_0 , and compare it to the 1-dimensional free electron model. Comment on why the free electron model appears to give a good approximation to the electron states in some metals.

[3 marks]

- (iii) (a) In GaAs the effective mass of an electron $m_n^* = 0.067m$. Using the answer to part (ii)(b), find the value of the potential U_0 in units of \hbar^2/ma for the conduction band in GaAs.

[2 marks]

[Total 20 marks]

SECTION C

5. The state of a two-level system can be described by a vector

$$|\psi\rangle = a_1 e^{-i\omega_1 t} |1\rangle + a_2 e^{-i\omega_2 t} |2\rangle, \quad (1)$$

where $|n\rangle$ are the eigenvectors of the two states ($n = 1, 2$) and ω_n are related to the energies of the states by $E_n = \hbar\omega_n$ ($E_2 > E_1$).

- (i) Under what circumstances can the coefficients a_n depend on time, i.e. $a_n = a_n(t)$? Name the approximation that allows us to use the time *independent* perturbation theory to find $a_n(t)$ and give its range of applicability. [4 marks]

Substituting $|\psi\rangle$ given by Eq.(1) into the time-dependent Schrödinger equation leads to a pair of differential equations:

$$\begin{aligned} i\frac{d}{dt}a_1(t) &= \Omega e^{+i(\omega-\omega_0)t} a_2(t) \\ i\frac{d}{dt}a_2(t) &= \Omega e^{-i(\omega-\omega_0)t} a_1(t) \end{aligned} \quad (2)$$

where ω is the angular frequency of an electron wave, $\omega_0 = \omega_2 - \omega_1$ and Ω is the Rabi angular frequency.

- (ii) State a solution of Eqs.(2) and show that it satisfies them (or solve the equations in any other way) for the case when an electromagnetic wave is resonant with the energy difference between the two levels. [4 marks]
- (iii) Suppose that the system is initially in state $|1\rangle$. Using your answer in part (ii) explain the meaning of the Rabi frequency. [4 marks]
- (iv) A laser emits pulses of 40 fs duration. The laser is tuned to a transition in an atomic system with the aim to transfer the system fully from the lower to the upper level. Assuming the dipole moment of the transition is equal to $-ea_0$ and the pulse envelope is square, calculate the following with an accuracy of 3 significant figures:
- (a) the Rabi angular frequency of the transition in SI and in atomic units, [3 marks]
 - (b) the electric field amplitude of the laser pulse in SI and in atomic units, [3 marks]
 - (c) the laser intensity of the pulse in SI units. [2 marks]

[Total 20 marks]

6. The configuration of a neon atom in the ground state is $\text{Ne } 1s^2 2s^2 2p^6$. Consider the outermost, 2p sub-shell of this atom.

- (i) Write down the 6 possible combinations of the (n, l, m_l, m_s) quantum numbers for this particular sub-shell. [2 marks]
- (ii) Write down the electron probability per unit solid angle for the state $|n \ l \ m_l \ m_s\rangle$ in the direction (θ, ϕ) in terms of a spherical harmonic. [2 marks]
- (iii) Using the formulae for the wavefunctions derive explicit expressions for the probability densities you have found in part (ii) for all the states considered in part (i). [3 marks]
- (iv) Calculate the sum of the probability densities you have found in part (iii) for the whole sub-shell. [3 marks]
- (v) Integrate the result of part (iv) over all angles. Explain the value you have obtained. [2 marks]
- (vi) Neon is a noble gas, which does not make chemical compounds. Explain this chemical unreactivity in terms of the result you found in part (iv). [3 marks]
- (vii) Four electrons are removed from the 2p sub-shell leaving the remaining electrons in a $1s^2 2s^2 2p^2$ configuration with zero total orbital angular momentum. For this new configuration do the following:
 - (a) Work out all possible combinations of total spin and total spin projection quantum numbers. [2 marks]
 - (b) Write down the possible term symbols and their multiplicity, listing them in the order of decreasing energies and indicating any degeneracies. Explain the energy order using the concept of Fermi heap or Fermi hole. [3 marks]

[Total 20 marks]