



UNIVERSITY OF
CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 1st June 2012 13.30 to 16.30

CHEMISTRY A: PAPER 1

Candidates should attempt all five questions

Where a question is divided into sections, the approximate division of marks between sections is indicated at the end of the question.

Linear graph paper is available if required.

Write on ONE side of the paper only.

The answers to each question should be returned separately.

A separate cover sheet for each question should be completed.

STATIONERY REQUIREMENTS

Graph paper (4 sheets)

Lined paper

Rough work pad

SPECIAL REQUIREMENTS

Chemistry master cover sheet

Department of Chemistry Data Book

<p>You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator.</p>
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A1

Answer *all* parts of the question.

- (a) Show that the (unnormalized) wave function

$$\Psi(x) = x \exp(-x^2/2)$$

is the first-excited state eigenfunction of the harmonic oscillator hamiltonian

$$\hat{H}(x) = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2 \quad (1)$$

and determine its eigenvalue.

- (b) (i) Explain what is meant by the term *quantum tunnelling*.
(ii) Calculate the tunnelling probability for the first-excited state of a harmonic oscillator. [Use the result: $\int_{\sqrt{3}}^{\infty} \exp(-x^2) dx = 0.01268$.]
(c) Consider a two-dimensional harmonic oscillator, with hamiltonian

$$\hat{H}(x, y) = \hat{H}(x) + \hat{H}(y)$$

where $\hat{H}(y)$ has the same form as $\hat{H}(x)$ in Eq. (1).

- (i) Show that the eigenfunctions of $\hat{H}(x, y)$ take the product form $\Psi_m(x)\Psi_n(y)$, where $\Psi_m(x)$ and $\Psi_n(y)$ are independent eigenfunctions of $\hat{H}(x)$ and $\hat{H}(y)$.
(ii) Hence show that the first excited state of $\hat{H}(x, y)$ is doubly degenerate, and sketch the two wave functions in the form of contour plots.
(iii) Calculate the region into which the two-dimensional system can tunnel, and indicate this on your sketch, identifying any preferential tunnelling directions. [You are not required to compute the tunnelling probability.]

Approximate division of marks: (a) 15%, (b) 45%, (c) 40%.

A2

Answer *all* parts of the question.

- (a) Explain briefly the purpose of *atomic units*, and give definitions of the atomic units of mass and charge.
- (b) The hamiltonian for the hydrogen atom can be written in atomic units as

$$\hat{H} = -\frac{1}{2} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{l}^2}{r^2} \right) - \frac{1}{r}$$

where

$$\hat{l}^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

- (i) Demonstrate that the hydrogen 1s orbital $\psi(r, \theta, \phi) = \pi^{-1/2} \exp(-r)$ is an eigenfunction of \hat{H} , and thus obtain a definition of the hartree (atomic unit of energy) in terms of the binding energy of a hydrogen 1s electron.
- (ii) Define the *radial probability distribution function* and use it to calculate the radius at which one is most likely to find an electron in a 1s orbital, thus obtaining a definition of the bohr (the atomic unit of length).
- (iii) Obtain an alternative definition of the bohr in terms of the expectation value of r for a hydrogen 1s electron.
- (c) (i) Explain, giving necessary commutators and eigenfunction equations, which components of the angular momentum of an electron in a hydrogen orbital can and cannot be measured precisely.
- (ii) Thus obtain a definition of the atomic unit of angular momentum in terms of the properties of a set of hydrogen 2p orbitals.

Approximate division of marks: (a) 10%, (b) 55%, (c) 35%.

[TURN OVER

A3

Answer *all* parts of the question.

- (a) Draw a diagram to show some of the transitions involved in the vibration-rotation spectrum of a diatomic molecule. Sketch the corresponding lines you expect to observe in the spectrum, clearly labeling the R branch and P branch. What factors determine the spacing between the lines and the amplitude of the transitions?
- (b) In the fundamental band of hydrogen fluoride, the following lines are observed in the P branch:

P(2)	P(3)	P(5)	P(6)
3877.89 cm ⁻¹	3833.96 cm ⁻¹	3741.71 cm ⁻¹	3693.75 cm ⁻¹

- (i) Determine the rotational constants B_0 and B_1 and comment on their relative values.
- (ii) Is the P(2) or P(5) line more intense at 300 K? Explain your reasoning.
- (iii) What is the equilibrium bond length of HF?
- (c) The fundamental absorption of HF occurs at 3961.42 cm⁻¹. The first overtone of this absorption was measured at 7750.81 cm⁻¹. Why is the first overtone observable and not at double the fundamental?
- (d) Assuming HF is a Morse oscillator calculate:
- (i) the equilibrium oscillation frequency
- (ii) the maximum vibrational level for HF
- (iii) the bond dissociation energy of HF.

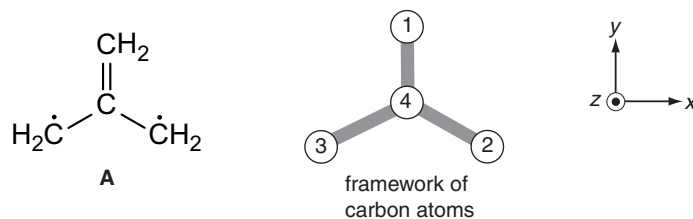
How will these values change if the hydrogen in HF is substituted for deuterium?

Approximate division of marks: (a) 30%, (b) 30%, (c) 10%, (d) 30%.

A4

Answer *all* parts of the question.

This question concerns the bi-radical A, whose structure is shown below. Throughout the question you should assume that the molecule is planar and that carbon atoms 1-3 are arranged in an equilateral triangle with atom 4 at its centre; use the numbering and axis system indicated.



- (a) Concentrating on just the carbon framework, what is the point group of this molecule? How many electrons are involved in the π system?
- (b) Construct symmetry orbitals from the four out-of-plane p orbitals in this molecule. For each symmetry orbital: (i) give the symmetry label, (ii) make a sketch of the orbital and (iii) give the normalized form of the orbital.
- (c) Using the simplest Hückel approximations, determine the energies of the molecular orbitals arising from overlap of these out-of-plane p orbitals. Draw up an energy level diagram of these MOs, giving each an appropriate symmetry label and indicating which are occupied. Find the coefficients of the atomic orbitals in the normalized, most bonding molecular orbital. Would you expect the electronic ground state of this molecule to be a triplet or a singlet?
- (d) Determine the total π energy of this molecule and compare this energy to that of a localized version of the bonding.

Approximate division of marks: (a) 10%, (b) 30%, (c) 40%, (d) 20%.

[TURN OVER

A5

Answer *all* parts of the question.

- (a) The intensity of a transition in the infra-red between the ground vibrational state ($v = 0$) and the first excited vibration state ($v = 1$) depends on, amongst other things, the value of the integral

$$\int \psi_0 \hat{\mu} \psi_1 d\tau,$$

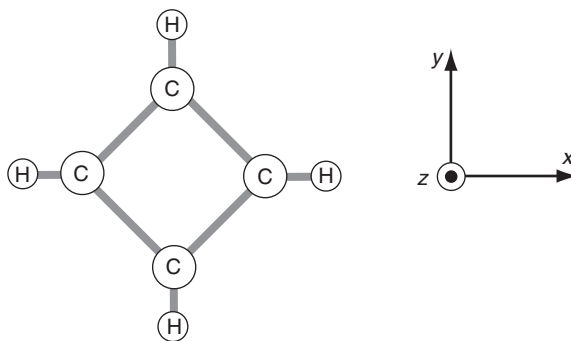
where ψ_0 is the ground-state wavefunction, ψ_1 is the wavefunction of the first excited state, and $\hat{\mu}$ is the dipole moment operator.

Using the properties of direct products, show that the fundamental transition of a given normal mode is only allowed if the normal mode transforms as the same irreducible representation as does one of the functions x , y or z .

State, without proof, the condition that this same transition gives rise to Raman scattering.

- (b) Determine the symmetries of all of the normal modes of cyclobutadiene, stating for which the fundamental transition is expected to be allowed in the infra-red, and for which of them the same transition is expected to give rise to Raman scattering.

You should assume that the molecule is planar, with a square arrangement of carbon atoms, as shown below. Use the axis system indicated.



How many features would you expect to see in (i) the infra-red and (ii) the Raman spectrum? How many of these features would be coincident? Rationalize your answer.

Approximate division of marks: (a) 25%, (b) 75%.

END OF PAPER



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NATURAL SCIENCES TRIPOS Part IB

Wednesday 6th June 2012 13.30 to 16.30

CHEMISTRY A: PAPER 2

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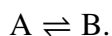
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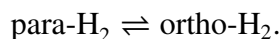
A6

Answer *all* parts of the question.

- (a) Hydrogen ^1H nuclei are fermions with spin $I = \frac{1}{2}$. Write down the acceptable nuclear spin functions for the $^1\text{H}_2^+$ molecule ion. Determine also the ground state electronic term symbol of this species.
- (b) Determine which rotational states J may be combined with each of the nuclear spin functions in part (a). Use your answer to explain the pattern of intensities that you would expect to observe in the rotational Raman spectrum of $^1\text{H}_2^+$.
- (c) Starting from an expression for the energy levels of a rigid rotor, derive an expression for the rotational partition function q_{rot} of a homonuclear diatomic in the high temperature limit.
- (d) Consider a generic process that interconverts two chemical species,



- (i) State, without proof, an expression for the equilibrium constant K_c of this reaction in terms of molecular partition functions, giving concise definitions of the symbols in the formula. Into what contributions may the partition functions be factorized, and what assumptions are necessary for this factorization to be made?
- (ii) Specialize your expression for K_c to the interconversion of para and ortho hydrogen,



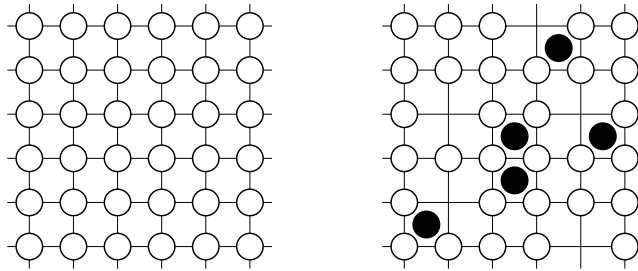
The rotational temperature of H_2 is $\theta_{\text{rot}} = 85 \text{ K}$. Calculate the ratio of ortho to para hydrogen at (a) 1000 K and (b) 50 K to two significant figures. Rationalize your results. What assumption has been made in this analysis?

Approximate division of marks: (a) 15%, (b) 25%, (c) 20%, (d) 40%.

A7

Answer **all** parts of the question.

- (a) (i) Show that, if a system is held at constant temperature and volume, the Helmholtz energy $A = U - TS$ decreases during a spontaneous process and therefore explain why A is a minimum at equilibrium.
- (ii) Write down the “bridge relation,” which expresses A in terms of the system partition function Q_N . Give a formula to define Q_N , explaining the meaning of the symbols.
- (b) A perfect crystal consists of N identical atoms occupying N lattice sites as illustrated in the left-hand diagram below. The structure also contains N interstitial sites that either may be vacant, or may accommodate a single atom that has moved from a lattice site, as illustrated in the right-hand diagram. Apart from single occupancy, there is no restriction on which interstitial sites are available to which atoms. The energetic cost of moving an atom from a lattice site to an interstitial site is $\Delta\varepsilon$, which is positive.



- atom occupying a lattice site
● atom occupying an interstitial site

- (i) Suppose that n atoms move from lattice sites to interstitial sites. By considering the number of ways that n particles can be chosen and distributed amongst n interstitial sites, show that the number of microstates available to the system is

$$\left(\frac{N!}{n!(N-n)!} \right)^2.$$

- (ii) Hence, show that the system partition function is

$$Q_N = \left(\frac{N!}{n!(N-n)!} \right)^2 \exp(-n\Delta\varepsilon/kT)$$

and derive an expression for the Helmholtz energy A .

[Qu. 7 continued on next page]

[TURN OVER]

[Continuation of Qu. 7]

- (iii) By minimizing A show that the equilibrium fraction of atoms at interstitial sites is

$$\frac{n}{N} = \frac{1}{\exp(\Delta\varepsilon/2kT) + 1}.$$

Approximate division of marks: (a) 30%, (b) 70%.

A8

Answer *all* parts of the question.

The semiconductor GaAs takes the zincblende crystal structure, defined by a face-centred cubic Bravais lattice with an atomic basis of one Ga atom and one As atom per primitive unit cell.

- (a) Given that the density of crystalline GaAs is 5.3176 g cm^{-3} , calculate the volume of the primitive unit cell, and hence determine the volume of the Brillouin zone.
- (b) Assuming valencies of 3 and 5 for Ga and As respectively, calculate the valence electron density of crystalline GaAs, and hence determine the volume of the free-electron Fermi sphere.
- (c) Comment upon the relative sizes of the free-electron Fermi sphere and the Brillouin zone, making reference to the likely number of occupied bands in the reduced-zone scheme. How might your answer differ if the crystal were to be isotropically compressed by an external force to a density slightly higher than that of its natural state, whilst remaining in the zincblende structure?
- (d) Given that the band gap between the highest occupied and lowest unoccupied electronic states in pure GaAs is 1.42 eV, use the Fermi-Dirac distribution to estimate the fractional occupancy of these states at 100 K, 300 K and 900 K (assuming no change in band gap with temperature). What entities are responsible for the conduction of electricity in this intrinsic semiconductor, and how does the temperature dependence of its conductivity compare with that of a typical metal?
- (e) When GaAs is doped with Si, the impurity atoms preferentially substitute for Ga atoms within the crystal structure. What type of charge carriers will dominate conduction in this case?

Approximate division of marks: (a) 20%, (b) 20%, (c) 20%, (d) 20%, (e) 20%.

[TURN OVER

A9

Answer *all* parts of the question.

Bloch's theorem may be expressed as

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_{\mathbf{k}}(\mathbf{r})$$

where \mathbf{r} indicates a position in real-space, \mathbf{R} is a real-space lattice vector, and \mathbf{k} is a good quantum number for an eigenfunction $\psi_{\mathbf{k}}(\mathbf{r})$ consistent with a periodic lattice.

- (a) State an alternative form of Bloch's theorem, and demonstrate that the validity of the form given above necessitates the validity of the one you have stated. Carefully define all terms appearing in your equations, including reference to any special properties that certain functions may have.
- (b) A certain two-dimensional crystal is defined by a square Bravais lattice (with lattice spacing a) and has an atomic basis comprising a single atom at each lattice point. The electronic eigenfunctions of this crystal, $\psi_{\mathbf{k}}(\mathbf{r})$, may be approximated as a linear combination of atomic orbitals (LCAO) of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{m,n} \exp(imk_x a + ink_y a) \chi_{mn}(\mathbf{r})$$

where the indices m and n indicate that the atomic orbital $\chi_{mn}(\mathbf{r})$ belongs to the atom found at the intersection of the m^{th} row and the n^{th} column of atoms, and where k_x and k_y are the x and y components of \mathbf{k} . Choosing two convenient primitive lattice vectors, \mathbf{a}_1 and \mathbf{a}_2 , determine a pair of primitive reciprocal lattice vectors, \mathbf{b}_1 and \mathbf{b}_2 . Hence demonstrate explicitly that the LCAO eigenfunctions satisfy the requirement that $\psi_{\mathbf{k}} = \psi_{\mathbf{k}+\mathbf{G}}$, where \mathbf{G} is a general reciprocal lattice vector.

- (c) By setting $\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2$, show that the Bloch functions of this system take the form

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{r})) \chi_{\mathbf{R}}(\mathbf{r})$$

where $\chi_{\mathbf{R}}(\mathbf{r}) \equiv \chi_{mn}(\mathbf{r})$, and where summation over \mathbf{R} may be taken to mean summation over both m and n .

Approximate division of marks: (a) 30%, (b) 40%, (c) 30%.

A10

Answer *all* parts of the question.

Useful optoelectronic devices may be made from materials having discrete spacings between their energy levels. In modern examples, such materials may include quantum dots comprising otherwise metallic elements, as well as the more traditional bulk semiconductors.

- (a) Describe the principle of operation of a light-emitting diode, and explain why such a device may be made from semiconducting materials such as GaAs and InP, but cannot generally be made from materials such as Si or Ge.
- (b) Optical measurements conducted on an extremely pure InP sample reveal that a series of relatively weak excitations of its electronic structure may take place at energies very slightly lower than its fundamental band gap energy. Explain the most likely origin of these excitations.
- (c) A Cu quantum dot is found to have a spacing of 0.25 eV between its lowest two energy levels. Estimate the number of atoms within the dot, assuming that it takes a cubic shape and that its density approximates that of bulk Cu (i.e. 8.920 g cm^{-3}).
- (d) How do the boundary conditions usually employed for bulk crystals differ from those implied in part (c) above, and what are the consequences for the spacing between energy levels?

Approximate division of marks: (a) 30%, (b) 20%, (c) 35%, (d) 15%.

END OF PAPER