

NATURAL SCIENCES TRIPOS Part 1B

Friday 3rd June 2011 13.30 to 16.30

CHEMISTRY A: PAPER 1

There are seven questions on this paper.

Candidates should attempt any 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.

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STATIONERY REQUIREMENTS

Graph paper x 4 sheets

Lined paper

Rough work pad

Cover sheets

SPECIAL REQUIREMENTS

Chemistry master cover sheet

Department of Chemistry Data Book

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A1 Answer all parts of the question

- (a) Give formulae defining what is meant by the term ‘Hermitian operator’. Why are Hermitian operators important in quantum mechanics?
- (b) The raising and lowering operators are defined by:

$$\hat{R} = \frac{1}{\sqrt{2}} \left(q - \frac{d}{dq} \right)$$

$$\hat{L} = \frac{1}{\sqrt{2}} \left(q + \frac{d}{dq} \right)$$

- (i) Determine whether these operators are Hermitian.
[You can assume that the limits of integration on q are $\pm \infty$.]
- (ii) Determine whether either of the linear combinations $\hat{R} + \hat{L}$ or $\hat{R} - \hat{L}$ is Hermitian.
- (c) The normalised ground and first-excited state harmonic oscillator wave functions are:

$$\psi_0(q) = \pi^{-1/4} e^{-q^2/2}$$

$$\psi_1(q) = \pi^{-1/4} \sqrt{2} q e^{-q^2/2}$$

Determine the effects of \hat{R} and \hat{L} on the ground state harmonic oscillator wave function $\psi_0(q)$, and thus evaluate the matrix element $\langle \psi_1 | q | \psi_0 \rangle$.

- (d) Show how to combine the operators \hat{R} and \hat{L} in such a way as to produce the Hamiltonian operator for the harmonic oscillator in terms of reduced units.

Approximate division of marks: (a) 10%, (b) 35%, (c) 30%, (d) 25%.

A2 Answer all parts of the question

- (a) The wave function $\Psi(r, \theta, \phi)$ describing the electron in a hydrogen atom satisfies the Schrödinger equation

$$-\frac{1}{2}\nabla^2\Psi(r, \theta, \phi) - \frac{1}{r}\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi) \quad [1]$$

where E is the energy, and atomic units have been used.

Use the results from the data book to show that the operator $-\frac{1}{2}\nabla^2$ can be written in the form

$$-\frac{1}{2}\nabla^2 = -\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{l}^2}{2r^2}$$

and give an expression for the operator \hat{l}^2 .

- (b) (i) Prove that the spherical harmonic

$$Y_{11}(\theta, \phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$

is an eigenfunction of \hat{l}^2 , and determine its eigenvalue.

- (ii) Prove that $Y_{11}(\theta, \phi)$ is normalised.

- (c) (i) Show that the product $\Psi(r, \theta, \phi) = Y_{11}(\theta, \phi)R(r)$ satisfies Eq. [1] above, provided that $R(r)$ satisfies an effective radial Schrödinger equation, which you should specify.
- (ii) Show that the function $R(r) = re^{-r/2}$ satisfies this effective radial Schrödinger equation and hence determine the energy of a hydrogen $2p$ orbital in atomic units.
- (d) A function $R(r) = r^2e^{-r/3}$ is suggested as the (unnormalised) radial component of a hydrogen $3p$ orbital. Demonstrate that this suggestion is erroneous *without* making use of the effective radial Schrödinger equation.

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

A3 Answer all parts of the question

Consider a one-dimensional system with Hamiltonian (in atomic units)

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

with

$$\begin{aligned} V(x) &= \infty \text{ for } & x < 0, & & x > 3 \\ V(x) &= 0 \text{ for } & 0 \leq x < 1, & & 2 < x \leq 3 \\ V(x) &= 1 \text{ for } & 1 \leq x \leq 2 \end{aligned}$$

A trial function is proposed to approximate the ground state wave function of this system, and is written in the form

$$\Psi(x) = c_1 \phi_1(x) + c_2 \phi_2(x)$$

where $\phi_1(x)$ and $\phi_2(x)$ are normalised particle-in-a-box eigenfunctions given by

$$\phi_n(x) = \sqrt{\frac{2}{3}} \sin\left(\frac{n\pi x}{3}\right)$$

- (a) Use the variation principle to show that the optimal values of the coefficients c_1 and c_2 satisfy the secular equations

$$\begin{aligned} (H_{11} - E)c_1 + H_{12}c_2 &= 0 \\ H_{21}c_1 + (H_{22} - E)c_2 &= 0 \end{aligned}$$

$$\text{where } H_{ij} = \int_0^3 \phi_i(x) \hat{H} \phi_j(x) dx .$$

- (b) (i) Calculate the matrix elements H_{11} and H_{22} .
(ii) Show without integrating explicitly that $H_{12}=0$.
- (c) Hence compute an estimate of the ground state energy of the system, and find the coefficients c_1 and c_2 .
- (d) Describe how one could obtain an improved estimate for the energy, E , by making use of additional particle-in-a-box eigenfunctions. Is it possible to obtain the exact value of the energy in this way?

Approximate division of marks: (a) 40%, (b) 35%, (c) 10%, (d) 15%.

A4 Answer all parts of the question

- (a) Contrast the features of harmonic and anharmonic oscillators in describing the vibration of a diatomic molecule. Sketch as quantitatively as you can the vibrational spectrum you would expect to observe in each case, naming individual features as appropriate.
- (b) Write down an expression for the vibrational energy levels of a diatomic molecule assuming the Morse potential, explaining the terms you use in your expression. Derive an expression for the equilibrium dissociation energy, \tilde{D}_e . How does the observed dissociation energy \tilde{D}_0 differ from \tilde{D}_e ?
- (c) Spectroscopic observations of the CN molecule in its ground ($X^2\Sigma$) and first excited ($A^2\Pi$) electronic states showed a number of IR transitions which have been assigned as shown in the table below:

	$v'' = 0 \leftarrow v' = 1$	$v'' = 1 \leftarrow v' = 2$
$X^2\Sigma$ electronic state	2042.42 cm^{-1}	2016.13 cm^{-1}
$A^2\Pi$ electronic state	1788.66 cm^{-1}	1762.90 cm^{-1}

Use this information to derive the fundamental vibrational frequencies, the anharmonicity constants, and hence the dissociation energies, \tilde{D}_e , for the X and A electronic states of the CN molecule.

- (d) Sketch the molecular orbital energy level diagram for the CN molecule and suggest suitable electronic configurations for the X and A electronic states, showing how they are consistent with the information given in part (c).

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

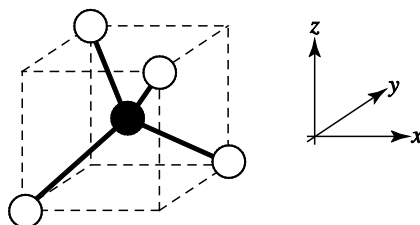
A5 *Answer all parts of the question*

- (a) (i) Identify the point group of the pyramidal molecule AH_3 , where A is a first-row element.
- (ii) What irreducible representations are spanned by the valence s and p orbitals on A and by the hydrogen $1s$ orbitals? Write down normalised forms of the hydrogen symmetry orbitals, using the symbols h_1 , h_2 and h_3 for the normalised atomic orbitals.
- (iii) Construct a qualitative molecular orbital diagram for this molecule, labelling the symmetry of the atomic and molecular orbitals.
- (iv) Is your MO diagram in (iii) consistent with the ammonia molecule having three equivalent N–H bonds? Justify your answer.
- (b) How would the molecular orbital diagram in part (a) differ qualitatively if the molecule were trigonal planar rather than pyramidal? Give the new point group of the molecule and the symmetry labels of the orbitals.
- (c) In the photoelectron spectrum of ammonia, the peak corresponding to the lowest ionisation energy shows a long vibrational progression with separation around 1000 cm^{-1} . Explain this observation.

Approximate division of marks: (a) 50%, (b) 30%, (c) 20%.

A6 Answer all parts of the question

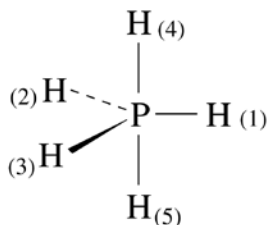
Consider the tetrahedral complex $[\text{NiCl}_4]^{2-}$ with the coordinate system given below. In this question you should ignore any π interactions between the Ni atom and the ligands.



- (a) Sketch the symmetry orbitals formed by the four ligand σ orbitals and state how they transform in point group T_d . Also state how the metal valence s , p , and d orbitals transform.
- (b) Construct and label the molecular orbital diagram of $[\text{NiCl}_4]^{2-}$. Mark the crystal field splitting Δ on your diagram.
- (c) (i) Identify the site symmetry of the ligands. Find the characters of the reducible representation spanned by the Cartesian displacements of a single ligand in this point group.
 (ii) Hence or otherwise, write down the reducible representation spanned by the Cartesian displacements of all four ligands in T_d and reduce it.
- (d) How many bands would you expect to see (i) in the infrared and (ii) in the Raman vibrational spectra of $[\text{NiCl}_4]^{2-}$?

Approximate division of marks: (a) 25%, (b) 25%, (c) 30%, (d) 20%.

A7 Answer all parts of the question



- (a) What is the point group of the trigonal bipyramidal PH_5 molecule shown above?
- (b) We may consider the bonding in PH_5 without using d orbitals. What representations are spanned by the phosphorus valence s and p orbitals and by the hydrogen $1s$ orbitals? Draw a labelled, schematic molecular orbital diagram for the molecule and sketch the occupied molecular orbitals.
- (c) Give expressions for the totally symmetric symmetry orbitals, numbering the hydrogen orbitals as in the diagram.
- (d) Set up the Hückel secular equations for the totally symmetric symmetry orbitals, assuming that $\alpha_{\text{H}} = \alpha_{\text{P}} = \alpha$, that $\beta_{\text{PH}} = \beta$ for both equatorial and axial hydrogens and that $\beta_{\text{HH}} = 0$. Solve the equations for the molecular orbital energies and find the coefficients of the atomic orbitals in the most strongly bonding molecular orbital.

Approximate division of marks: (a) 5%, (b) 30%, (c) 15%, (d) 50%.

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part 1B

Wednesday 8th June 2011 13.30 to 16.30

CHEMISTRY A: PAPER 2

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A8 Answer all parts of the question

Throughout this question you should ignore symmetry effects.

- (a) Starting from the ‘bridge relationship’ $A = -kT \ln Q_N$, derive the following expression for the internal energy of a system consisting of N non-interacting indistinguishable molecules with molecular partition function q . Be sure in your derivation to explain each step carefully.

$$U = NkT^2 \frac{1}{q} \left(\frac{\partial q}{\partial T} \right)_N.$$

- (b) The rotation of a diatomic can be modelled using the rigid rotor energy levels

$$E_J = BJ(J+1) \quad J = 0, 1, 2, \dots$$

where B is the rotational constant and each level has a degeneracy of $(2J+1)$. Show that in the limit $kT \gg B$ the rotational partition function is well-approximated by

$$q_{\text{rot}} = \left(\frac{T}{\theta_{\text{rot}}} \right).$$

where θ_{rot} , the characteristic rotational temperature, is given by $\theta_{\text{rot}} = B/k$.

Be sure in your derivation to explain each step carefully.

Go on to use this form of q_{rot} to find an expression for the molar internal energy due to rotation; comment on your answer.

- (c) The expression derived in (b) is a poor approximation for the partition function at temperatures comparable to θ_{rot} . In this region a better approximation is

$$q_{\text{rot}} = \left(\frac{T}{\theta_{\text{rot}}} \right) \left(1 + \frac{1}{3} \frac{\theta_{\text{rot}}}{T} + \frac{1}{15} \left(\frac{\theta_{\text{rot}}}{T} \right)^2 \right).$$

For $\text{H}_2(\text{g})$ at a temperature of 100 K, and for which $\theta_{\text{rot}} = 85.5$ K, find the numerical values of q_{rot} , $(\partial q_{\text{rot}} / \partial T)_V$ and the molar internal energy due to rotation. Compare your values of q_{rot} and the molar internal energy with those found using the expressions in (b).

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

A9 *Answer all parts of the question*

For this question you may need the following relationships

$$dA = -SdT - pdV \quad A = -kT \ln Q_N \quad U = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right),$$

where Q_N is the partition function of the system.

- (a) Explain in words how the energy levels of a “particle in a box” can be used to model the translational energy levels of a molecule in a (non-interacting) gas, and derive the translational partition function given below

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V,$$

where m is the mass of the molecule and V is the volume of the container in which it is held.

- (b) Derive an expression for the contribution to the molar internal energy of the gas made by these translational energy levels.
- (c) Using your result from (a) in conjunction with the relevant relationships given at the beginning of the question, derive an expression for the pressure exerted by a gas consisting of non-interacting atoms. Comment on your result.

Question A9 continues over the page.

Question A9 continued

- (d) In a real gas the molecules interact with one another and also have finite size. The van der Waals gas is a simple model for such a gas, and it can be shown that for such a gas the partition function of the system is

$$Q_N = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} (V - Nb)^N \exp\left(\frac{aN^2}{VkT} \right),$$

where N is the number of atoms (or molecules), and a and b are the two van der Waals constants; a is a measure of the interaction between the molecules and b is a measure of the volume of the molecules. These constants are characteristic of a particular gas, are positive and are independent of both temperature and volume.

Derive an expression for (i) the molar internal energy of a van der Waals gas and (ii) the pressure exerted by the gas. Compare your answers to the results from (b) and (c).

Approximate division of marks: (a) 20%, (b) 20%, (c) 25%, (d) 35%.

A10 *Answer all parts of the question*

- (a) Starting from the 'bridge relationship', $A = -kT \ln Q_N$, show that the chemical potential μ_i of species i in a mixture of ideal gases is given by

$$\mu_i = -kT \ln \frac{q_i}{N_i} + \epsilon^{0,i},$$

where q_i is the molecular partition function, N_i is the number of molecules, and $\epsilon^{0,i}$ is the energy of the electronic ground state of i .

- (b) By expressing the partition function in terms of the volume independent partition function f_i (where $f_i = q_i / V$), show that the equilibrium constant for the reaction

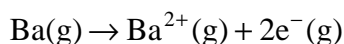


can be expressed as

$$K_c = \frac{f_B (f_C)^2}{f_A (c^0)^2} \exp(-\Delta \epsilon^0 / kT)$$

where c^0 is the standard concentration. In your answer, be sure to define $\Delta \epsilon^0$.

- (c) Determine the values of the equilibrium constant K_c for the following ionization process at a temperature of 2000 K.



The first and second successive ionisation energies of Ba are $0.509 \text{ MJ mol}^{-1}$ and $0.972 \text{ MJ mol}^{-1}$, respectively.

Assuming that Ba gas is present at a pressure of 0.01 bar, estimate the (fractional) degree of ionization of Ba to Ba^{2+} . Comment on your answer.

Approximate division of marks: (a) 30%, (b) 25%, (c) 45%.

A11 *Answer all parts of the question*

A certain binary compound, AB, crystallises with a simple hexagonal Bravais lattice, having a primitive unit cell spanned by the following lattice vectors:

$$\mathbf{a}_1 = a(1/2, -\sqrt{3}/2, 0) \quad \mathbf{a}_2 = a(1/2, \sqrt{3}/2, 0) \quad \mathbf{a}_3 = c(0, 0, 1)$$

In fractional coordinates, with respect to the above vectors, the atoms of the basis are located at:

$$\begin{aligned} \text{A:} & \quad (0, 0, 0) \quad \text{and} \quad (0, 0, 1/2) \\ \text{B:} & \quad (1/3, 2/3, 1/4) \quad \text{and} \quad (2/3, 1/3, 3/4) \end{aligned}$$

The atoms may be assumed to behave as hard spheres, with the A atoms close-packed within the basal plane, and the atomic radius of the B atoms, r_B , smaller than that of the A atoms, r_A . Given that the ratio of atomic radii, $\rho = r_B/r_A$, is sufficiently large that nearest-neighbour A and B atoms just touch, it may be shown that the distance between their centres is

$$d = r_A + r_B = \sqrt{\frac{a^2}{3} + \frac{c^2}{16}}$$

- (a) Show that the ratio c/a can be written as:

$$\frac{c}{a} = \sqrt{\frac{4}{3}(3(1 + \rho)^2 - 4)}$$

- (b) Evaluate the primitive reciprocal lattice vectors of this crystal, and hence determine the size and shape of its first Brillouin zone.
- (c) Given $\rho = \sqrt{3} - 1$, make use of the expression provided in part (a) to express the average valence electron density of this crystal, n , in terms of only the basal-plane lattice constant, a and the total number of valence electrons per primitive unit cell, N .
- (d) Hence determine the maximum value of N for which a free-electron Fermi sphere would fit entirely within the First Brillouin Zone of this crystal. Comment on the likely suitability or otherwise of the nearly-free-electron model as an approximation for the electronic properties of this material. You may quote without proof any expression for the Fermi wavenumber of the free-electron model.

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

A12 *Answer all parts of the question*

- (a) The valence electron density distribution of a crystalline solid must display the same periodicity as the underlying Bravais lattice. Demonstrate that this constraint implies that the electronic wavefunctions, $\psi_{\mathbf{k}}(\mathbf{r})$, must satisfy Bloch's theorem, stated as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

and identify the crucial constraints that apply to the wavevector, \mathbf{k} , and to the Bloch function, $u_{\mathbf{k}}(\mathbf{r})$.

- (b) Show that the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r})$$

may be re-written as the Bloch equation

$$\left[\frac{\hbar^2}{2m} (-i\nabla + \mathbf{k})^2 + V(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r})$$

and explain (in outline) why the latter may conveniently be solved using a Fourier expansion approach, while the former may not.

- (c) Show that substitution of a spatially constant potential and spatially constant Bloch function, $u_{\mathbf{k}}(\mathbf{r})$, into the Bloch equation above necessarily leads to a parabolic (quadratic) energy-wavevector relationship, while substitution of any sufficiently strongly-localised Bloch function into the same equation leads to an electronic energy that is only weakly dependent upon the wavevector.
- (d) Describe the qualitative distinctions between the band structures of metals, intrinsic semiconductors, insulators and semi-metals, explaining how these account for characteristic differences in electrical conductivity and commenting upon the effect of varying temperature.

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

A13 Answer all parts of the question

- (a) Explain, with examples, the qualitative difference between direct gap and indirect gap semiconductors. Discuss the implications for the absorption of photons in the two cases.
- (b) A sample of silicon is substitutionally doped with boron to a concentration of 10^{14} cm^{-3} , creating a dispersionless acceptor level located 0.04 eV above the valence band maximum. Assuming the Fermi level lies midway between the valence band maximum and this acceptor level, estimate the density of free carriers within the valence band at 300 K. Comment on how this compares with the intrinsic free-carrier density of silicon of 10^{10} cm^{-3} at 300 K and explain qualitatively how the situation will change at progressively higher temperatures.
- (c) Sketch the valence and conduction band edges of an *n*-doped and of a *p*-doped semiconductor, before and after bringing them together to form a *p-n* junction. Include the Fermi levels and the donor/acceptor levels on your diagrams. Use these diagrams to explain the rectification of current by a *p-n* junction diode, and indicate, with reasons, under which conditions the diode may function as an LED.
- (d) The III-V semiconductors GaAs, GaP and GaN have band gaps of 1.42 eV, 2.26 eV and 3.40 eV, respectively. Suggest, with quantitative reasoning, which of these materials is most suitable for the fabrication of a violet-light LED (wavelength in the 380-450 nm range).

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

A14 *Answer all parts of the question*

- (a) Explain qualitatively, with the aid of suitable band structure diagrams, the concept of a Peierls distortion in a one-dimensional solid, paying particular attention to the implications for electrical conductivity in chain polymers.
- (b) Outline how the band structure of graphene differs from that of graphite, and discuss how it might be expected to vary under the influence of externally applied (i) isotropic in-plane strain, and (ii) uniaxial in-plane strain.
- (c) If a large-radius, single-walled carbon nanotube is considered to comprise a sheet of graphene rolled into a long cylinder, what additional constraint must the electronic wavefunctions satisfy? Assuming free-electron-like behaviour in all regards *other* than this constraint, what qualitative behaviour would one expect from the density of states?
- (d) How does the bonding in diamond differ from that in graphene, graphite and the nanotube? What are the consequences for its band structure?

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

[END OF PAPER]