UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Wednesday 27th May 2020   **Three hours**

CHEMISTRY A: PAPER 1

Candidates should attempt all five questions; where a question is divided into parts, candidates should answer all parts.

Each question is marked out of 20. Where a question is divided into parts, the *approximate* number of marks available for each part is indicated thus   **[*n*]**

Write on ONE side of the paper only.

Start each question on a new sheet of paper.

Be sure to write the question number on each sheet and if your answer to a question covers several pages, please number the pages. If you know it, also write your candidate number (blind grade number, BGN) on each page.

Students are permitted to use an approved calculator and will need a copy of the *Department of Chemistry Data Book* to hand.

A1

The Hamiltonian of an harmonic oscillator, written in the scaled coordinate q, is

$$\hat{H}_0 = -\tfrac{1}{2}\frac{d^2}{dq^2} + \tfrac{1}{2}q^2$$

The normalized ground-state wavefunction of $\hat{H}_0$ is

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

(a)   In the following calculations (i)–(iv) use the ground-state wavefunction, $\psi(q)$.

   (i)   Show that $\psi(q)$ is an eigenfunction of $\hat{H}_0$ and verify that the energy eigenvalue is $E_0 = \tfrac{1}{2}$. **[4]**

   (ii)   Evaluate the expectation values of q and q^2. You may need the integral **[3]**

$$\int_{-\infty}^{+\infty} q^2 e^{-q^2}\, dq = \tfrac{1}{2}\sqrt{\pi}$$

   (iii)   Show that the expectation value of the potential energy, $V_0 = \langle \tfrac{1}{2}q^2 \rangle$, is $\tfrac{1}{4}$. **[2]**

   (iv)   Using the result from (i) and (iii), and without detailed calculations, state the expectation value of the kinetic energy, T_0. **[1]**

(b)   The harmonic Hamiltonian $\hat{H}_0$ given at the start of the question is now modified by adding a term linear in q:

$$\hat{H} = -\tfrac{1}{2}\frac{d^2}{dq^2} + \overbrace{\left(\tfrac{1}{2}q^2 - aq\right)}^{\hat{V}(q)}$$

where a is a parameter which is positive.

A possible trial wavefunction for the ground state of $\hat{H}$ is

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

where b is a variational parameter. Note that this is just the function $\psi(q)$ shifted by b and that the function is still normalized.

   (i)   For the trial wavefunction $\phi(q)$ show that the expectation value of the potential $V(q)$ is given by

$$\langle V(q) \rangle = V_0 + \tfrac{1}{2}b^2 - ab$$

where V_0 is expectation value of the harmonic potential found in (a) (iii). **[6]**

[Hint: start by rewriting both $V(q)$ and $\phi(q)$ in terms of q' where $q' = q - b$.]

   (ii)   The expectation value of the kinetic energy for $\phi(q)$ is the same as found in (a) (iv).

Use the variational principle to determine b as a function of a. Hence evaluate the corresponding estimate of the ground-state energy. **[3]**

A2

The Hamiltonian of a rigid rotor is

$$\hat{H}_0 = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

where ϕ is the angular coordinate and I is the moment of inertia. A wavefunction $\psi(\phi)$ for this system must satisfy the periodic boundary condition

$$\psi(\phi + 2n\pi) = \psi(\phi)$$

where n is an integer. A consequence of this is when normalizing the wavefunction or computing expectation values the range of integration of ϕ is from 0 to 2π.

A set of useful trigonometric identities are given at the end of this question.

(a) (i) Show that $\psi_c = N_c \cos \phi$ and $\psi_s = N_s \sin \phi$, where N_c and N_s are normalization factors, are eigenfunctions of $\hat{H}_0$ and determine the energy eigenvalues. **[4]**

  (ii) Determine the normalization factors N_c and N_s; hence write down the two wavefunctions in their normalized forms. **[2]**

  (iii) Find the *normalized* ground-state wavefunction ψ_0 of the hamiltonian $\hat{H}_0$. Give its energy and verify that $\psi_0(\phi)$ satisfies the periodic boundary condition given above. **[4]**

[Qu. **A2** continued on next page]

[Continuation of Qu. **A2**]

(b) The rigid-rotor Hamiltonian $\hat{H}_0$ is extended by adding a potential energy term which results in the rotation being hindered.

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \overbrace{-A\sin(2\phi)}^{\hat{V}(\phi)}$$

where A is a parameter determining the magnitude of the hindering potential; A is positive.

(i) Show that for the two wavefunctions ψ_c and ψ_s the expectation value of the potential, $\langle V(\phi)\rangle = \langle \psi|\hat{V}(\phi)|\psi\rangle$, is zero. **[6]**

(ii) An approximate wavefunction for this system can be found from the linear combination

$$\psi_{approx} = c_c\psi_c + c_s\psi_s$$

where c_c and c_s are coefficients. Values for these coefficients and the corresponding energies E can be found by setting up and solving the relevant secular equations

$$\begin{pmatrix} H_{cc} - E & H_{cs} \\ H_{sc} & H_{ss} - E \end{pmatrix}\begin{pmatrix} c_c \\ c_s \end{pmatrix} = 0$$

where the matrix elements are

$$H_{cc} = \langle \psi_c|\hat{H}|\psi_c\rangle \qquad H_{ss} = \langle \psi_s|\hat{H}|\psi_s\rangle \qquad H_{cs} = H_{sc} = \langle \psi_c|\hat{H}|\psi_s\rangle$$

Using your results from (b) (i) determine the values of these matrix elements and hence find the lowest energy of the system. **[4]**

Trigonometric identities

$$\cos^2\phi = \tfrac{1}{2}(1 + \cos 2\phi) \quad \sin^2\phi = \tfrac{1}{2}(1 - \cos 2\phi) \quad \sin\phi\cos\phi = \tfrac{1}{2}\sin 2\phi$$

A3

(a) The potential energy curve of a diatomic molecule can be described using the harmonic potential or, to a better approximation, the Morse potential.

    (i) Write down the expressions for the harmonic potential $V_H(r)$ and the Morse potential $V_M(r)$ as a function of the bond length r. Explain the significance of all the parameters. **[5]**

    (ii) Make careful sketches of both potentials as a function of x, the extension of the bond length from its equilibrium value. Label the sketches with any relevant parameters.

    Comment on the key differences between the two potentials as models for bond stretching. **[5]**

(b) The vibrational energy levels (expressed in cm^{-1}) associated with the Morse potential are given by

$$\tilde{\varepsilon}_v = (v + \tfrac{1}{2})\tilde{\omega} - (v + \tfrac{1}{2})^2\tilde{\omega}x_e$$

    (i) Use this to derive an expression for the dissociation energy $\tilde{D}_e$ measured from the bottom of the potential energy well. **[4]**
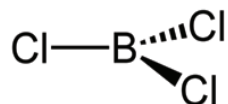
    (ii) Why, in practice, might this value be different from the experimentally measured dissociation energy? **[2]**

    (iii) Comment on how $\tilde{D}_e$ changes when the force constant in the Morse potential changes, including any relevant equations. **[4]**

A4

The boron trichloride molecule (BCl_3) is trigonal planar. It is used as a strong Lewis acid in the synthesis of organic compounds.


(a)   (i)   State the point group of this molecule.   **[1]**

    (ii)   Divide the 3p atomic orbitals on the Cl atoms into three convenient sets, explaining very briefly your choice.   **[2]**

    (iii)   Find and reduce the representation spanned by each set.   **[4]**

    (iv)   By drawing analogies with relevant cartesian functions, find the symmetry orbitals resulting from each set. Give a sketch of each symmetry orbital, label it with the appropriate irreducible representation, and give the orbital in its normalised form.   **[5]**

(b)   (i)   Construct a molecular orbital energy diagram for BCl_3 using only the 2s and 2p atomic orbitals on the boron atom, and only the 3p atomic orbitals on the chlorine atoms. Give each MO the appropriate label and identify any that are non-bonding.   **[6]**

    The exact energy ordering of the bonding and anti-bonding orbitals is not required, nor are sketches of the MOs.

    (ii)   As a Lewis acid, BCl_3 forms adducts with tertiary amines NR_3. Adduct formation is often accompanied by a change in B–Cl bond length.

    Use your MO diagram to deduce whether you would you expect the B–Cl bond length to change on adduct formation and, if so, in what way. Give brief reasons for your answer.   **[2]**

A5

This question is about the π molecular orbitals of the oxylate (ethanedioate) dianion $C_2O_4{}^{2-}$ shown below. The anion is planar and all of the oxygen atoms are equivalent. You should use the axis system and numbering shown.

The point group of this molecule is $\mathcal{D}_{2h}$
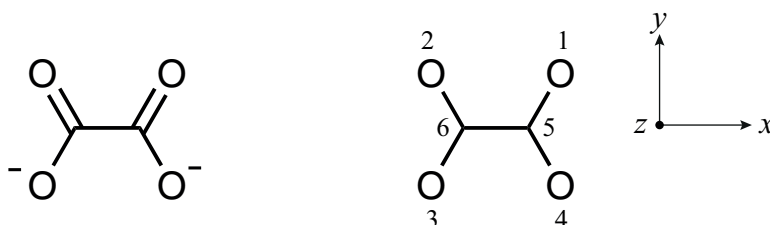
(a)   (i)   Find and reduce the representation spanned by the four oxygen p_z atomic orbitals. **[2]**

(ii)   Give the normalized form of the symmetry orbitals arising from these atomic orbitals. Make a sketch of each, clearly labelling it with the relevant irreducible representation. **[4]**

(iii)   Give the normalized form of the symmetry orbitals arising from the two carbon p_z atomic orbitals. Make a sketch of each, clearly labelling them with the relevant irreducible representation. **[2]**

(b)   For the following calculations use the simplest Hückel approximations. Take the energy of the oxygen orbitals as $\alpha_O = \alpha + \beta$, that of the carbon orbitals as $\alpha_C = \alpha$, and assume that the interaction between any pair of adjacent atomic orbitals is represented by β.

(i)   Determine the energies of the symmetry orbitals found in (a) (ii) and (iii). **[2]**

(ii)   Determine the energies of *all* of the molecular orbitals in terms of α and β. Values of the orbital coefficients are *not* required. **[6]**

(iii)   Draw an MO energy diagram, roughly to scale, labelling all of the MOs appropriately. **[1]**

(iv)   Determine which of these MOs are occupied for the oxylate dianion, and for the related species C_2O_4. What differences and similarities do you predict for these two species on the basis of your MO diagram? **[3]**

END OF PAPER

UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Tuesday 2nd June 2020   **Three hours**

CHEMISTRY A: PAPER 2

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A6

(a) For an ideal gas the translational contribution of N molecules (or atoms) to the entropy is given by

$$S_{\text{trans}} = Nk \ln q_{\text{trans}} - Nk \ln N + Nk + \frac{U_{\text{trans}}}{T} \tag{1}$$

where q_{trans} is the translational partition function, U_{trans} is the translational contribution to the internal energy, T is the temperature and k is Boltzmann's constant. The translational partition function for a molecule or atom of mass m is given by

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

where V is the volume and h is Planck's constant.

  (i) Show that the standard molar entropy of a monotomic ideal gas is given by

$$S_{\text{m}}^{\circ} = R\left[\ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{RT}{p^{\circ}}\right\} - \ln N_{\text{A}} + \frac{5}{2}\right]$$

  where R is the gas constant, p° is the standard pressure, and N_{A} is Avogadro's constant. In your derivation be sure to explain any approximations or assumptions you make. **[6]**

  (ii) Explain concisely how Eq. 1 is modified to give the contribution of internal modes of motion to the entropy. **[3]**

(b) (i) For $^{12}\text{C}^{32}\text{S}_2$ the rotational constant is found to be 0.109 cm^{-1} and the lowest frequency normal mode is at 399 cm^{-1}. The molecular mass is 75.94 m_{u}.

  Compute the standard molar entropy of $^{12}\text{C}^{32}\text{S}_2$ in the gas phase at 200 K, assuming the gas to be ideal. State any further assumptions and approximations you make. **[8]**

  (ii) Comment on how your calculation might be different at a higher temperature, say 300 K. **[3]**

A7

(a) The probability P_m of a system occupying microstate m with energy E_m is given by the canonical probability distribution function

$$P_\mathrm{m} = \frac{1}{Q_\mathrm{N}}\, e^{-E_\mathrm{m}/kT} \qquad Q_\mathrm{N} = \sum_\mathrm{m} e^{-E_\mathrm{m}/kT}$$

where the sum is over all microstates of the sytem, k is Boltzmann's constant, T is the temperature and Q_N is the partition function of the system.

The internal energy of a system described by this distribution is given by

$$U = \sum_\mathrm{m} P_\mathrm{m} E_\mathrm{m}$$

(i) Show that

$$U = kT^2 \frac{1}{Q_\mathrm{N}} \left(\frac{\partial Q_\mathrm{N}}{\partial T} \right)_V$$

[2]

(ii) Show that, if the system consists of N non-interacting identical (indistinguishable) particles the energy is given by

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

In your answer be sure to explain carefully each step and to define the quantity q. **[2]**

[Continuation of Qu. **A7**]

(b) Consider a system consisting of N identical non-interacting particles each of which has three non-degenerate energy levels with energies 0, ε_1, and ε_2.

(i) Show that the internal energy of this system is given by

$$U = \frac{N\left(\varepsilon_1\, e^{-\varepsilon_1/kT} + \varepsilon_2\, e^{-\varepsilon_2/kT}\right)}{1 + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}}$$

[2]

(ii) In each of the following cases deduce the value of, or appropriate expression for, U; comment on the physical interpretation of each:

1. $\varepsilon_1 \gg kT$ and $\varepsilon_2 \gg kT$
2. $\varepsilon_1 \ll kT$ and $\varepsilon_2 \ll kT$
3. $\varepsilon_1 \ll kT$ and $\varepsilon_2 \gg kT$

[5]

(iii) Hence sketch a plot of U as a function of temperature for the case $\varepsilon_2 \gg \varepsilon_1$, from zero up to a temperature such that $kT \gg \varepsilon_2$. Label any features of interest on the plot. **[2]**

(iv) Without any detailed calculations sketch the corresponding plot of the constant volume heat capacity C_V against T. **[2]**

(c) Now consider the case where $\varepsilon_1 = \varepsilon_2 = \varepsilon$. By using the result from (b)(i) it follows that

$$U = \frac{2N\varepsilon\, e^{-\varepsilon/kT}}{1 + 2e^{-\varepsilon/kT}}$$

(i) From this expression for U derive an expression for the constant volume heat capacity C_V. **[2]**

(ii) Use the expression you have derived to determine the heat capacity in the limits $kT \ll \varepsilon$ and $kT \gg \varepsilon$. **[2]**

(iii) Hence make a sketch of how you expect C_V to vary with T (no further calculations are expected). **[1]**

A8

(a) Consider the hypothetical second order reaction

$$A + BC \longrightarrow AB + C$$
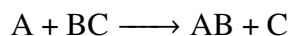
where A, B and C represent individual atoms.

Show, with concise explanations, how the application of transition state theory leads to an expression for the second order rate constant k_{2nd} of the form

$$k_{2nd} = \frac{1}{c^\circ} k_{1st} K^*$$

In your answer be sure to define all of the quantities in the above expression. **[4]**

(b) Write down an expression for K^* for the above reaction using appropriate partition functions. **[2]**

(c) Show how the expression for K^* leads to the Eyring expression

$$k_{2nd} = \frac{1}{c^\circ} \frac{k_B T}{h} K^\ddagger$$

In your answer you should make explicit the difference between K^* and $K^\ddagger$. **[4]**

(d) The rate determining step of a particular reaction involves the breaking of a C–H bond. Estimate as quantitatively as you can, making clear any assumptions, what the effect of deuterating the relevant hydrogen would be on the reaction rate constant at 298 K. **[6]**

[You may assume a typical C–H stretch frequency of 3000 cm^{-1}]

(e) Suppose that in the reaction in (a) the reactant molecule BC was instead an atom D with the same mass as BC. *Estimate* the likely order of magnitude change that this would make on the pre-exponential factor (*A* factor) of the reaction, briefly explaining your approach. **[4]**

A9

(a) Shown below is a part of a hexagonal two-dimensional Bravais lattice, the lattice vectors of which are $\boldsymbol{a}_1 = a[1, 0]$ and $\boldsymbol{a}_2 = \frac{1}{2}a[-1, \sqrt{3}]$; nearest neighbours in this lattice are all spaced by a.
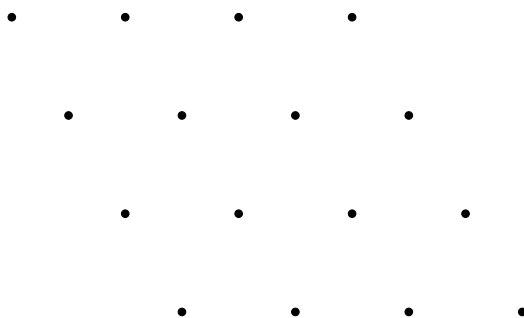
    (i) Imagine that a circle of radius r is placed at each lattice point and that r is then increased until the circles on nearest neighbours touch. Calculate the packing fraction of this arrangement. **[2]**

    (ii) Now imagine that a basis of two atoms is attached to each lattice point $[x_i, y_i]$ such that the first atom is at $[x_i, y_i]$ (i.e. on the lattice point) and the second atom is at $[x_i, y_i + c]$. Calculate the value of c needed to generate the hexagonal net shown below; the atoms at $[x_i, y_i + c]$ are shown by open circles. **[3]**
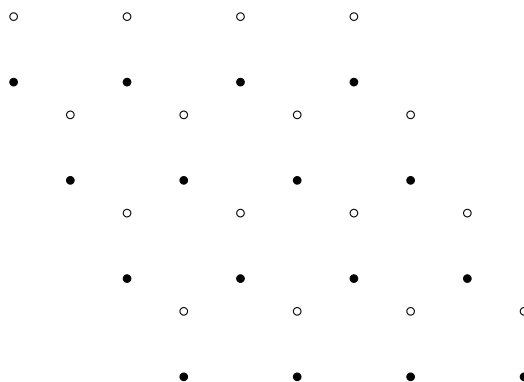
    (iii) As in (i) imagine that a circle of radius r is placed at each position occupied by an atom in the hexagonal net. Calculate the maximum packing fraction in such a case (i.e. when circles on nearest neighbours touch). **[3]**

[Continuation of Qu. **A9**]

(b) The reciprocal lattice units vectors b_j, $j = 1, 2$ and those of the real-space lattice a_i, $i = 1, 2$, are related by

$$a_i . b_j = 2\pi\delta_{ij} \qquad \text{where } \delta_{ij} = 1 \text{ if } i = j \text{ and } = 0 \text{ otherwise}$$

For the hexagonal lattice the reciprocal lattice vectors are

$$b_1 = b[1, \frac{1}{\sqrt{3}}] \qquad b_2 = b[0, \frac{2}{\sqrt{3}}]$$

(i) Find the value of b in terms of a. **[2]**

(ii) Shown below is a section of the reciprocal lattice of the hexagonal real-space lattice; nearest neighbour reciprocal lattice points are separated by $2b/\sqrt{3}$.
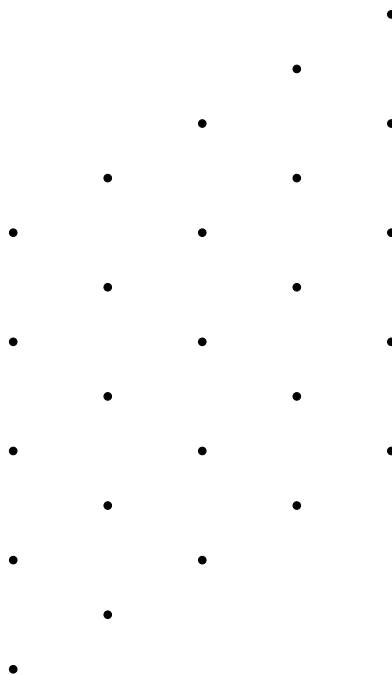
A copy of the above is provided for you. On this, use a geometric construction to find the first Brillouin zone [be sure to return this diagram with your answer and write your candidate number on it].

What shape is the zone, and what is its area in terms of b and also in terms of a? **[3]**

[Qu. **A9** continued on next page]

[Continuation of Qu. **A9**]

(iii) What is the radius of the Fermi circle (in terms of b) which just touches the closest edge of the first Brillouin zone? **[3]**

Also express you answer in terms of a.

(iv) The density of Born von Karman allowed states in two dimensions is $L_1 L_2 A_c/(2\pi)^2$, where there are L_1 and L_2 units cells along the $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ directions, respectively, and A_c is the area of the real-space unit cell.

Calculate how many electrons per unit cell will result in a Fermi circle with the radius you have calculated in (iii). Comment on your answer. **[4]**

A10

(a) The Fermi–Dirac distribution gives the probability $f(E)$ that a state with energy E will be occupied

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

where T is the temperature, k_B is the Boltzmann constant, and E_F is the energy of the Fermi level.

A simple model for a semiconductor is that there is a valence band (VB) which is fully occupied by electrons in the limit of zero temperature and a conduction band (CB) which is unoccupied in this same limit.

In this question it is assumed that the semiconductor has a constant density of states D_0 within the VB and the CB; elsewhere the density of states is zero. The width of both the CB and VB is E_b, and the band gap is E_g.

(i) Make a sketch of the band structure described above showing the density of states along the vertical axis and energy on the horizontal axis; label your diagram with relevant quantities. **[2]**

(ii) What do you understand by the terms *density of states* and *density of occupied states*? **[2]**

(iii) Explain why, at $T = 0$, it follows that $N = 2D_0 E_b$, where N is the number of electrons in the valence band. **[2]**

(iv) Assuming that the Fermi–Dirac distribution applies, derive an expression for the total number of electrons occupying states within the CB at temperature T. **[3]**

You will need the integral

$$\int_{x_1}^{x_2} \frac{1}{e^{a(x-x_0)} + 1} \, dx = (x_2 - x_1) + \frac{1}{a} \left[\ln\left(1 + e^{a(x_1 - x_0)}\right) - \ln\left(1 + e^{a(x_2 - x_0)}\right) \right]$$

(v) Use your expression to find the *fraction* of the electrons which have been promoted to the conduction band for the case $T = 600$ K, $E_g = 0.50$ eV, and $E_b = 0.50$ eV. **[3]**

Comment on your result.

[You may find it useful to use $k_B = 8.62 \times 10^{-5}$ eV K^{-1}.]

[Qu. **A10** continued on next page]

[Continuation of Qu. **A10**]

(b) This part of the question is concerned with the spectroscopy of semiconductor materials whose electronic structure can be modelled as consisting of a valence band (VB) and a conduction band (CB) separated by a band gap.

  (i) Briefly, and with the aid of a suitable diagram, explain the difference between a *direct band gap* and an *indirect band gap*. **[3]**

  (ii) State the selection rule for optical transitions between the VB and the CB in terms of the wavevectors of the states involved.

  Explain briefly how the involvement of *phonons* can make a transition corresponding to the energy of the band gap possible for indirect band gap materials. **[2]**

  (iii) For a particular material the wavevector of the lowest energy state of the CB has $k = 9.0 \times 10^9$ m^{-1}; the highest energy state of the VB has a wavevector of zero.

  Calculate the speed of propagation of the phonons needed to make the lowest energy transition between the VB and the CB possible at 298 K. **[3]**

END OF PAPER

Figure to be handed in together with the answer to Question A9