NATURAL SCIENCES TRIPOS Part 1B

Friday 29th May 2009   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

A1 *Answer all parts of the question*

(a)   The Schrödinger equation for a harmonic oscillator is

$$-\frac{1}{2}\frac{d^2\Psi_v(q)}{dq^2} + \frac{1}{2}q^2\Psi_v(q) = E_v\Psi_v(q)$$

where q is a scaled position coordinate.

(i)   By substituting the ground state wave function $\Psi_0(q) = \exp(-q^2/2)$ into this equation, demonstrate the meaning of the terms *eigenfunction* and *eigenvalue*.

(ii)   Write down (but do not evaluate) expressions for the uncertainties in the position Δq and the energy ΔE for a system described by $\Psi_v(q)$.

(b)   One of the excited state wave functions for the harmonic oscillator can be written

$$\Psi_{ex}(q) = (q^2 - a)\exp(-q^2/2)$$

where a is a positive constant, which remains to be determined.

(i)   Deduce which particular excited state this function describes, without making use of the Schrödinger equation.

(ii)   Substitute $\Psi_{ex}(q)$ into the Schrödinger equation, to determine its energy and the value of the constant a.

(iii)   Now determine a without making use of the Schrödinger equation, but using instead your knowledge of $\Psi_0(q)$ and the properties of the $\Psi_v(q)$.

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

A2 *Answer all parts of the question*

(a) The spherical harmonics $Y_{lm}(\theta,\phi)$ satisfy the equations:

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

$$\hat{l}_z Y_{lm}(\theta,\phi) = \hbar m Y_{lm}(\theta,\phi) \quad (2)$$

(i) Which physical observables do the operators $\hat{l}^2$ and $\hat{l}_z$ correspond to, and what are the restrictions on the quantum numbers l and m?

(ii) Write down (but do not derive) expressions for the commutators $[\hat{l}_x,\hat{l}_y]$, $[\hat{l}_y,\hat{l}_z]$, $[\hat{l}_z,\hat{l}_x]$ and $[\hat{l}_i,\hat{l}^2]$ (where i is x, y or z). Hence explain why $Y_{lm}(\theta,\phi)$ cannot also satisfy equations analogous to eqn. (2) above in which $\hat{l}_z$ is replaced by $\hat{l}_x$ or $\hat{l}_y$.

(iii) Give the explicit mathematical form of the operator $\hat{l}_z$ and use this to obtain an expression for the ϕ-dependent part of $Y_{lm}(\theta,\phi)$.

(b) The hamiltonian for a hydrogen atom can be written in scaled coordinates as

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

Show that the eigenfunctions have the form $R_{nl}(r)Y_{lm}(\theta,\phi)$, and derive the equation satisfied by $R_{nl}(r)$.

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

A3 *Answer all parts of the question*

The molecular orbitals of a diatomic molecule can be approximated by the expression

$$\Psi = c_1\phi_1 + c_2\phi_2$$

where ϕ_1 and ϕ_2 are atomic orbitals centred on each nucleus.

(a) Use the variation principle to derive the secular equations

$$(H_{11} - E)c_1 + H_{12}c_2 = 0$$
$$H_{21}c_1 + (H_{22} - E)c_2 = 0$$

where $H_{ij} = \int \phi_i \hat{H} \phi_j d\tau$. You may assume that ϕ_1 and ϕ_2 are normalised and have zero overlap, and that c_1 and c_2 are real.

(b) (i) Calculate the bonding and anti-bonding energy levels for the case that $H_{11} = \alpha + \beta$, $H_{22} = \alpha - \beta$, and $H_{12} = H_{21} = \beta$, where α and β are empirically determined constants. State clearly any assumptions you make about the signs of α and β.

(ii) Without calculating c_1 and c_2, give approximate sketches of the form of the bonding and anti-bonding molecular orbitals, assuming that ϕ_1 and ϕ_2 are *s*-orbitals.

(c) ϕ_1 and ϕ_2 are modified to include a variable parameter γ, such that the matrix elements now satisfy,

$$H_{11} = \frac{\alpha}{\gamma} + \beta\gamma; \quad H_{22} = \frac{\alpha}{\gamma} - \beta\gamma$$
$$H_{12} = H_{21} = \beta\gamma$$

where α and β are constants. Obtain the best estimate of the ground state energy using these parameterised orbitals. How might this estimate be further improved?

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

A4 *Answer all parts of the question*

(a) An astronomer suspects that the molecular species $[HCO]^+$ exists in a particular galactic cloud and wishes to find evidence for this by detecting the microwave (i.e. pure rotation) emission spectrum from this species. The astronomer consults a friendly theoretical chemist who uses *ab initio* calculation to predict that the molecule will be linear with a C−H bond length of 1.086 Å and a C−O bond length of 1.087 Å
Using these data (and assuming integer masses) predict the form of the microwave emission spectrum, expressing your result in cm^{-1} and in GHz.

(b) It is important to know which of these transitions will be the strongest so as to have the greatest chance of detecting it. Making the simplest assumptions about the factors which affect line intensities, predict the frequencies of the three strongest emissions, given that the astronomer believes that the temperature of the cloud is around 100 K.

(c) The friendly theoretical chemist also calculates that the normal modes of $[HCO]^+$ will have frequencies of 3896 cm^{-1}, 2814 cm^{-1}, and 729 cm^{-1}. Using these data, explain what you would expect to see in the IR spectrum of this molecule; include a discussion of any fine structure.

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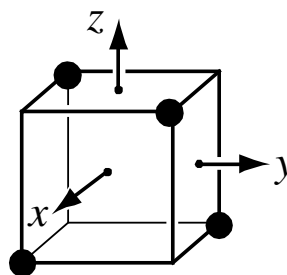
[TURN OVER

A5 *Answer all parts of the question*

(a)   What is the point group of the methane molecule?

(b)   Find the characters of the representations generated by the following sets of orbitals, and reduce them.

  (i) the carbon 2s atomic orbital

  (ii) the carbon 2p orbitals

  (iii) the sp^3 hybrids:

$$\eta_1 = \tfrac{1}{2}\,(2s + 2p_x + 2p_y + 2p_z)$$

$$\eta_2 = \tfrac{1}{2}\,(2s - 2p_x - 2p_y + 2p_z)$$

$$\eta_3 = \tfrac{1}{2}\,(2s + 2p_x - 2p_y - 2p_z)$$

$$\eta_4 = \tfrac{1}{2}\,(2s - 2p_x + 2p_y - 2p_z)$$

  (iv) the four hydrogen 1s orbitals

  (v) the four C−H stretching vibrations.

(c)   For the isolated carbon atom, the non-vanishing Hückel matrix elements are $\langle 2s|\hat{H}|2s\rangle = \alpha_s$ and $\langle 2p_x|\hat{H}|2p_x\rangle = \langle 2p_y|\hat{H}|2p_y\rangle = \langle 2p_z|\hat{H}|2p_z\rangle = \alpha_p$. Hence derive the secular matrix for the isolated carbon atom in the two basis sets $\{2s, 2p_x, 2p_y, 2p_z\}$ and $\{\eta_1, \eta_2, \eta_3, \eta_4\}$.

(d)   Write down the energy eigenvalues and the eigenvectors of the secular matrix derived in (c) in the $\{2s, 2p_x, 2p_y, 2p_z\}$ basis. Show that in the $\{\eta_1, \eta_2, \eta_3, \eta_4\}$ basis the eigenvectors become $\tfrac{1}{2}(1, 1, 1, 1)$, $\tfrac{1}{2}(1, -1, 1, -1)$, $\tfrac{1}{2}(1, -1, -1, 1)$, and $\tfrac{1}{2}(1, 1, -1, -1)$. By substituting these eigenvectors into the secular equations, show that the eigenvalues of the secular matrix in the hybrid orbital basis are the same as in the atomic orbital basis.

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

A6 *Answer all parts of the question*
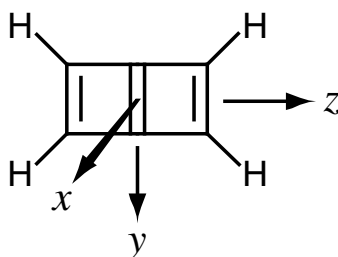
(a)   What is the point group of the above molecule, C_6H_4? Identify the site group for every atom in a distinct chemical environment.

(b)   How does the function *xyz* transform in this point group?

(c)   Derive symmetry orbitals for the p-π system and sketch them, identifying the corresponding irreducible representation in each case.

(d)   Calculate the MO energies for the π system and draw a labelled MO energy level diagram.

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

A7 *Answer all parts of the question*

(a)   For each of the following molecules, determine the point group and the
        symmetries of the C−H stretching modes.

formaldehyde   ethene   naphthalene
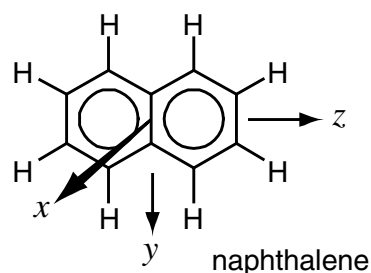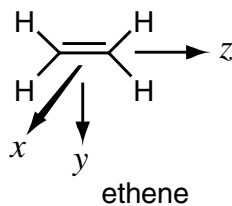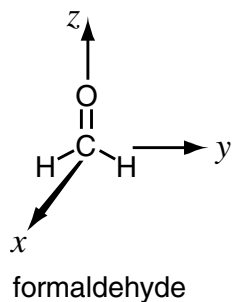
(b)   For the formaldehyde molecule, sketch symmetry adapted linear combinations
        of the C−H stretches, identifying the appropriate irreducible representations in
        each case.

(c)   Identify the allowed infra-red and Raman transitions from the ground state of
        ethene to all doubly-excited vibrational states derived from the C−H stretches.

(d)   What is the Laporte selection rule? Explain how 'd-d' transitions between
        molecular orbitals derived primarily from metal d orbitals can be permitted by
        symmetry in (i) octahedral and (ii) tetrahedral transition metal complexes.

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

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part 1B

Wednesday 3rd June 2009   13.30 to 16.30

CHEMISTRY A: PAPER 2

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Department of Chemistry Data Book

A8 *Answer all parts of the question*

(a)   Derive the expression for the molecular partition function for translation in 3D for a gas of non-interacting, indistinguishable atoms.
Define all parameters you use and state any assumptions you make clearly.
Hence show that this partition function is of the form:

$$q_{tr,3D} = B\, m^{3/2}\, T^{3/2}$$

Where m is the relative molecular mass and T the absolute temperature. Give the expression for the constant, B, in terms of the fundamental parameters, k_B, the Boltzmann constant, h, Planck's constant and the volume, V, of the gas.

(b)   State the relationship between the canonical partition function, Q_N, and molecular partition function, q, for N non-interacting, indistinguishable atoms.

Starting from the 'bridge' relation for the Helmholtz energy, $A = -k_B T \ln Q_N$, and the master equation for dA, derive the expression for the molar entropy of a gas of non-interacting, indistinguishable atoms, in terms of the molecular partition function, q.
Define clearly all parameters you introduce and any approximations you make.

(c)   Use the results in part (a) and (b) to show that the molar entropy of a gas of non-interacting, indistinguishable atoms is of the form:

$$S = C + D \ln m^{3/2}$$

and hence find expressions for constants C and D.
  (You may assume the electronic partition function is unity.)

[Question A8 continues over the page]

A8 continued

(d)   Use the data below and the relationship in part (c) to estimate the standard
        molar entropy of argon at 300K.

	Molar mass / g mol^{-1}	Molar Entropy at 300K / J K^{-1} mol^{-1}
Kr	83.8	164.1
Xe	131.3	169.7

Molar mass of Ar is 40 g mol^{-1}.

(e)   Explain why the experimental molar entropy of nitrogen molecules, N_2, at
        300K is significantly greater than the value given by the expression in part (c).

Approximate division of marks: (a) 25%, (b) 25%, (c) 20%, (d) 20%, (e) 10%.

A9 *Answer all parts of the question*

(a)   State the relationship between the partition function of a system, Q_N, and the Helmholtz free energy, A. Clearly define any other parameters you use.
Hence show that the chemical potential, μ, of an ideal gas of N particles each with partition function q is given by:

$$\mu = -k\,T\,\ln(q/N)$$

State clearly any approximations you use.

(b)   For mixtures of species, chemical potentials are of the form:

$$\mu_i = -kT\ln(q_i/N_i) + \varepsilon_i^0$$

Where there are N_i particles of species i each with partition function q_i.
By consideration of the change in Gibbs free energy, show that the equilibrium constant, K_p, of the reaction:

$$\text{H}_2\,(g) + \text{Br}_2\,(g) \rightleftharpoons 2\,\text{HBr}\,(g)$$

is of the form:

$$K_p = \frac{(q_{\text{HBr}}^\circ)^2}{q_{\text{H}_2}^\circ\, q_{\text{Br}_2}^\circ}\exp\left(\frac{-\Delta\varepsilon_\circ}{kT}\right)$$

Where q_i° denotes the partition function for one mole of species i in the standard state. Clearly state the meaning of the parameters ε_i^0 and $\Delta\varepsilon_\circ$ and their relation.

(c)   Using the data in the table below determine the equilibrium constant, K_p, for the reaction $\text{H}_2\,(g) + \text{Br}_2\,(g) \rightleftharpoons 2\text{HBr}$ at 500K.

	Molar Mass / g mol^{-1}	Electronic ground state	θ_{vib} / K	θ_{rot} / K	D_e / cm^{-1}
H$_2$	2	$^1\Sigma_g^+$	6332	85.3	38,231
Br$_2$	158	$^1\Sigma_g^+$	463	0.12	16,033
HBr	80	$^1\Sigma^+$	3787	12.0	31,556

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

A10 *Answer all parts of the question*

The adsorption of hydrogen molecules onto a surface may occur by two routes: dissociative or non-dissociative adsorption:

$$\text{Dissociative: } H_2(g) \rightleftharpoons 2H(ads)$$

$$\text{Non-dissociative: } H_2(g) \rightleftharpoons H_2(ads).$$
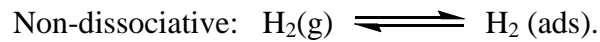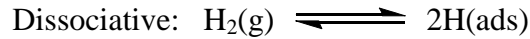
(a) In the non-dissociative route molecules adsorb and occupy a single surface site with partition function q_{H_2}. The number of ways of arranging N separate molecules onto M surface sites is:

$$\frac{M!}{N!(M-N)!}$$

State the partition function of the system, Q_N, in terms of q_{H_2}, N and M.
Show that the Helmholtz free energy of N adsorbed molecules is:

$$A = kT\,[-N\ln q_{H_2} - M\ln M + N\ln N + (M-N)\ln(M-N)]$$

stating clearly any assumptions you make.
Show that the chemical potential of the adsorbed layer is given by:

$$\mu(\text{ads}) = k_B T\left[-\ln q_{H_2} + \ln\left(\frac{\theta}{1-\theta}\right)\right]$$

where θ is the fraction of occupied surface sites.

By considering the chemical potential of a gas of these species at pressure, P_{H_2}, show that the Langmuir isotherm can be derived:

$$\theta = \frac{b\left(P_{H_2}/P_\circ\right)}{1 + b\left(P_{H_2}/P_\circ\right)}$$

where P_o is the standard pressure of the gas at the given temperature and give the expression for b, a pressure independent constant.

A10 continued

(b)   In the dissociative route molecules adsorb as separate atoms, where each atom occupies a single surface site with partition function q_H.

Find the Helmholtz free energy and chemical potential of N molecules dissociatively adsorbed. Show that the fractional coverage of atoms follows the following relation:

$$\theta = \frac{b'\left(P_{H_2}/P_\circ\right)^{\frac{1}{2}}}{1+b'\left(P_{H_2}/P_\circ\right)^{\frac{1}{2}}}$$

Where P_{H_2} is the pressure of hydrogen gas and give an expression for b' which is a pressure independent constant.

Approximate division of marks: (a) 60%, (b) 40%.

A11 *Answer all parts of the question*

(a) The Schrödinger equation for a single electron moving in a *constant* potential V and confined to a finite one-dimensional space of length L is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Explain why the standard "particle in a box" approach $[\psi(0) = \psi(L) = 0]$ does not provide a satisfactory basis for an approximate description of solid state electronic structure and show how this difficulty may be circumvented by an appropriate choice of boundary conditions.

(b) Hence obtain expressions for the wavefunctions, energy levels and momenta of the quantum states, pointing out how they differ from the corresponding quantities derived *via* the standard "particle in a box" approach.

(c) Consider a chain of 10^{22} *monovalent* atoms spaced 0.3 nm apart. Estimate for the wavevector and energy of the highest occupied orbital.

$$\left[\frac{\hbar^2}{2m_e} = 6\times10^{-39}\,\text{m}^4\,\text{kg}\,\text{s}^{-2}\right]$$

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

A12 *Answer all parts of the question*

(a)   Give a concise description of the Hall effect. On the basis of free electron theory obtain an expression for the Hall coefficient (R_H) making clear any assumptions or approximations that are used in your derivation.

(b)   The experimentally observed and calculated (free electron model) Hall coefficients and Fermi energies for Na and Be are shown in the tables below.

	R_H (free electron calc.) / $m^3 C^{-1}$	R_H (observed) / $m^3 C^{-1}$
Na	-24.1×10^{-11}	-25.0×10^{-11}
Be	-2.5×10^{-11}	$+24.4 \times 10^{-11}$

	E_F (free electron calc.) / kJ mol^{-1}	E_F (observed) / kJ mol^{-1}
Na	305	338
Be	1332	1303

Account for these data in detail making reference to the concepts of Brillouin zone and Fermi surface.

(c)   Explain with reasons whether or not you expect Be to be a good electronic conductor.

Approximate division of marks: (a) 45%, (b) 45%, (c) 10%.

A13 *Answer all parts of the question*

(a)   Explain what is meant by the terms intrinsic semiconductor, n-type semiconductor, and p-type semiconductor. Account for the location of the Fermi level in each of these three cases.

(b)   Outline how statistical mechanics may be used to obtain an expression for n_e, the number density of conduction electrons in an undoped semiconductor crystal with bandgap E_g at temperature T.

(c)   A silicon crystal characterized by a bandgap of 1.0 eV is doped with 10^{21} Sb atoms m^{-3} giving rise to impurity levels that lie 0.02 eV from the nearest band edge. At 300 K the electron and hole mobilities are $\mu_e = 0.13$ m^2 V^{-1} s^{-1} and $\mu_h = 0.05$ m^2 V^{-1} s^{-1}, respectively. Estimate the electrical conductivity of this crystal at 300 K, making clear any approximations or assumptions, given that for pure un-doped Si at 300 K the number density of conduction electrons, n_e, is 10^{15} m^{-3}.

(d)   Estimate the temperature at which the above Sb-doped Si crystal would exhibit approximately equal intrinsic and extrinsic conductivities.

$k_B = 8.6$ x 10^{-5} eV K^{-1}
$e = 1.6$ x 10^{-19} C

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

A14 *Answer all parts of the question*

(a)   With the aid of suitable diagrams, explain how a contact potential difference develops when a junction is formed between p-type and n-type semiconducting materials.

(b)   Describe how such a p-n junction behaves (i) under forward bias and (ii) under reverse bias.

(c)   Explain how light emission may occur at a p-n junction, pointing out and explaining any factors that may inhibit such radiative transitions.

(d)   The table below gives the temperature dependence of the electrical conductivity of a certain doped semiconductor. What *quantitative* information can you deduce from it? Indicate qualitatively how you would expect the electrical conductivity to vary at temperatures below ~ 300 K.

T / K	300	400	600
σ / m^{-1} V^{-1} s^{-1} C	18	20	500

$k_B = 8.6 \times 10^{-5}$ eV K^{-1}

Approximate division of marks: (a) 20%, (b) 10%, (c) 20%, (d) 50%.

[END OF PAPER]