

**The Handbook of Mathematics, Physics and
Astronomy Data is provided**

KEELE UNIVERSITY

EXAMINATIONS, 2011/12

Level III

Tuesday 1st May 2012, 13:00 – 15:00

PHYSICS/ASTROPHYSICS

PHY-30009

QUANTUM PHYSICS OF ATOMS AND MOLECULES

Candidates should attempt to answer THREE questions.

A sheet of useful information can be found on page 7.

NOT TO BE REMOVED FROM THE EXAMINATION HALL

1. The potential between two atoms in a molecule can be approximated using the following perturbation of the harmonic oscillator potential, $V(x) = \frac{1}{2}kx^2$:

$$V'(x) = V(x) - 5kx^3/r_0,$$

where x is the displacement from the equilibrium separation r_0 , and k is the spring constant for the molecular bond.

The energy eigenfunctions for the harmonic oscillator potential are given on page 7.

- (a) Describe briefly the key concepts that are used to develop time-independent perturbation theory as a method to analyse perturbed potentials. [15]
- (b) Show that the first-order correction to the ground state energy due to this perturbation is 0. [15]
- (c) Calculate an expression for ψ'_0 , the energy eigenfunction for the ground state of the potential $V'(x)$ in terms of r_0 , k , a and the reduced mass μ . [40]
- (d) Discuss how transitions between vibrational energy levels can give rise to Raman scattering of laser light and describe the appearance of the resulting Raman scattered spectrum for a typical gas at room temperature. [30]

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2. The expectation value for the separation of the electrons in ground state of helium is

$$\langle |\mathbf{r}_p - \mathbf{r}_q| \rangle = \frac{16\pi\epsilon_0\hbar^2}{5e^2m_e}.$$

- (a) Why is there no triplet state (3S_1) in the ground state of helium? [10]

- (b) Use the value of $\langle |\mathbf{r}_p - \mathbf{r}_q| \rangle$ above to estimate the ground state energy of helium. [15]

- (c) The effective nuclear charge, Z' , can be used to make the following improved estimate for the energy of the ground state,

$$E_{GS} = \left(Z'^2 - \frac{27}{8}Z' \right) E_R,$$

where $E_R = 13.61$ eV is the Rydberg energy.

- i. Describe the phenomenon that is accounted for by using the effective nuclear charge. [10]
 - ii. Describe the key concepts that lead to the *variational principle* as a method to estimate the ground state energy. [20]
 - iii. Apply the variational principle to find the optimum value of Z' and so calculate an improved estimate of E_{GS} . [15]
- (d) Explain why the 3S_1 triplet has a lower energy than the 1S_0 singlet in the $1s2p$ excited state of helium. [30]

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3. Calcium atoms have two optically active electrons. In one possible excited state these electrons have the configuration $4s^1 4p^1$.
- (a) Sketch the energy levels for these electrons using spectroscopic notation to label each state, e.g., 3P_2 . Your sketch should indicate the correct ordering of the energy levels according to Hund's rules and the relative spacing of different levels. You do not need to provide an energy scale for your sketch. [25]
- (b) The 3P multiplet of the $4s^1 4p^1$ state has experimentally determined energies (relative to the ground-state) of 1879.57 meV, 1886.04 meV and 1899.17 meV. Show that the splitting of these energy levels is consistent with an LS-coupling scheme. [30]
- (c) State the selection rules that govern allowed transitions between the $4s^1 4p^1$ state and the 3P multiplet of the $3d^2$ state. Hence, list all possible transitions between the $4s^1 4p^1$ state and the 3P multiplet of the $3d^2$ state that are not forbidden. [25]
- (d) i. Which transitions from part (c) will be split into the fewest number of components by the Zeeman effect? [5]
- ii. For any one of the transitions from part (d) i., use a sketch to show how the Zeeman effect splits this spectral line. Your sketch should show the correct number and relative spacing of the spectral lines. [15]

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4. The rotational energy levels of a linear molecule with moment of inertia \mathcal{I} are given by

$$E = \frac{\hbar^2}{2\mathcal{I}} J(J + 1),$$

where $J(= 0, 1, 2 \dots)$ is the rotational quantum number.

- (a) State the selection rule for allowed rotational transitions. [5]

- (b) The interatomic distance in $^{14}\text{N}^{16}\text{O}$ is 115 pm. Calculate the frequency of the allowed rotational transition of $^{14}\text{N}^{16}\text{O}$ that has the longest wavelength, and show that the approximation $h\nu/k_{\text{B}}T \ll 1$ is valid at $T = 60$ K. [35]

- (c) Hence show that the partition function Z may be approximated by

$$Z = \frac{2\mathcal{I}}{\hbar^2} k_{\text{B}}T. \quad [30]$$

- (d) Which of the rotational levels in $^{14}\text{N}^{16}\text{O}$ is most heavily populated at 60 K? [30]

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5. (a) Give an account of the covalent bond in the case of the H_2^+ molecular ion. Include in your discussion the significance of the symmetry of the electron eigenfunctions, and the conditions for the stability of H_2^+ . [60]
- (b) Extend your discussion to the case of the H_2 molecule; include in your discussion the significance of electron spins for the formation of the covalent bond. [40]

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Quantum Mechanics formulae

Energy eigenfunctions for the quantum harmonic oscillator

For the potential $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x$ and particle mass m .

n	Energy	Eigenfunction
0	$E_0 = \frac{1}{2} \hbar\omega$	$\psi_0(x) = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} e^{-x^2/2a^2}$
1	$E_1 = \frac{3}{2} \hbar\omega$	$\psi_1(x) = \left(\frac{2}{a\sqrt{\pi}}\right)^{1/2} \left(\frac{x}{a}\right) e^{-x^2/2a^2}$
2	$E_2 = \frac{5}{2} \hbar\omega$	$\left(\frac{1}{2a\sqrt{\pi}}\right)^{1/2} \left[1 - 2\left(\frac{x}{a}\right)^2\right] e^{-x^2/2a^2}$

Notes: $\omega = \sqrt{k/m}$, $a = \sqrt{\hbar/m\omega}$. These energy eigenfunctions are normalized.

Standard definite integrals

$$\int_{-\infty}^{\infty} x^{2n} e^{-x^2/\alpha^2} dx = \frac{1 \times 3 \times \dots \times (2n-1)}{2^n} \alpha^{2n+1} \sqrt{\pi} \quad \text{for } n = 1, 2, 3, \dots$$