KEELE UNIVERSITY

DEGREE EXAMINATIONS, 2009

Level 3 (PRINCIPAL COURSE)

Tuesday 5 May 2009, 16:00 - 18:00

PHYSICS/ASTROPHYSICS

PHY-30009

QUANTUM PHYSICS OF ATOMS AND MOLECULES

Candidates should attempt to answer THREE questions.

Tables of physical and mathematical data may be obtained from the invigilator.

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1. Consider a particle in the following infinite square well potential.

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < a \\ \infty & x \geq a \end{cases}$$

The energy eigenfunctions of this potential are

$$\psi(x) = \begin{cases} 0 & x \leq 0 \\ \sqrt{\frac{2}{a}} \sin(n\pi x/a) & 0 < x < a \\ 0 & x \geq a \end{cases}$$

with energy $E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}$, $n = 1, 2, 3, \ldots$.

(a) An arbitrary wavefunction $\Psi(x,t)$ can be expressed as

$$\Psi(x,t) = \sum_{i=1}^{n} c_i \psi_i(x) e^{-iE_i t/\hbar}.$$

Give a physical interpretation of the constants c_i [20]

(b) The potential is perturbed by a field of the form

$$v(x) = \begin{cases} 0 & x \leq 0 \\ \epsilon x/a & 0 < x < a \\ 0 & x \geq a \end{cases}$$

Calculate an approximate correction to the ground state energy, E_1, in the case $\epsilon \ll E_1$. [40]

(c) Explain why the restriction $\epsilon \ll E_1$ is required for the approximation in part (b) to be valid. [15]

(d) The particle is in the ground state at times $t < 0$. The perturbation in part (b) is "turned on" at time $t = 0$, i.e.,

$$\epsilon = 0, \quad t < 0$$
$$\epsilon = C, \quad t \geq 0$$

where $C > 0$ is a constant. Discuss qualitatively whether this perturbation is likely to lead to the emission of a photon. [25]

You may find the following integral to be useful

$$\int x \sin^2(bx)\, dx = \frac{x^2}{4} - \frac{x \sin(2bx)}{4b} - \frac{\cos(2bx)}{8b^2} + C$$

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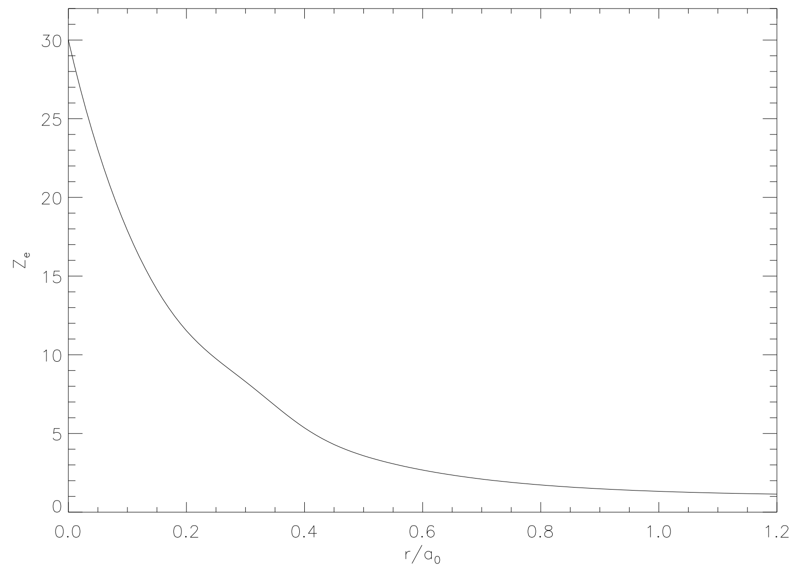
2. The figure below shows the effective nuclear charge, Z_e, for a zinc atom (Z=30) in its ground state calculated using the Hartree method (self consistent field method).



(a) Describe and explain the behaviour of $Z_e(r)$ for large values of r and for small values of r. [20]

(b) The radial eigenfunction for electrons in the 2p sub-shell of zinc in its ground state peaks near $r = 0.2a_0$. Estimate the energy required to remove one electron from this sub-shell and comment on the accuracy of your method. [40]

(c) Describe the main features of an experiment that can be used to measure the energy required to remove one electron from the 2p sub-shell of zinc. [20]

(d) Explain why spin-orbit coupling has a much larger effect on the energy level in zinc than in hydrogen. [20]

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3. Calcium atoms have two optically active electrons. In one possible excited state these electrons have the configuration $(3s)^1(4d)^1$.

   (a) Sketch the energy levels for these electrons using spectroscopic notation to label each state, e.g., $^3D_2$. 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 you sketch. [25]

   (b) The ^3D multiplet of the $(3s)^1(4d)^1$ state has experimentally determined energies (relative to the ground-state) of 4680.764 meV, 4681.219 meV and 4681.911 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 $(3s)^1(3p)^1$ state and the ^3P multiplet of the $(3s)^1(3d)^1$ state. Hence, list all possible transitions from the $(3s)^1(3p)^1$ state to the ^3P multiplet of the $(3s)^1(3d)^1$ state that are not forbidden. [25]

   (d) Explain which transition from part (c) will be split into the lowest number of components by a weak external magnetic field? How many components will the Zeeman effect produce in this case? [20]

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4. (a) Give an account of the covalent bond in the case of the H_2^+ molecular ion; include in your discussion the significance of even and odd electron eigenfunctions, and the conditions for the stability of the H_2^+ ion. [50]

   (b) Extend your discussion to the case of the H_2 molecule; include in your discussion the significance of electron spins on the formation of the covalent bond. [50]

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

   (a) State the selection rule for allowed rotational transitions. [10]

   (b) The interatomic distance in $^{13}C^{16}O$ is 1.128×10^{-10} m. Calculate the frequency of the allowed rotational transition $^{13}C^{16}O$ that has the longest wavelength, and show that the approximation $h\nu/k_BT \ll 1$ is valid at $T = 100$ K. [35]

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

$$Z = \frac{2\mathcal{I}}{\hbar^2}\, k_BT$$ [25]

   (d) Which of the rotational levels in $^{13}C^{16}O$ is most heavily populated at 100 K? [30]