NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET Institutt for fysikk

Faglig kontakt under eksamen: Ingjald Øverbø, tel. 73 59 18 67, eller 97012355

## EKSAMEN I TFY4215 KJEMISK FYSIKK OG KVANTEMEKANIKK 26. mai 2006

kl. 09.00 - 13.00

Tillatte hjelpemidler: Godkjent kalkulator;

Rottmann: Matematisk formelsamling; Øgrim & Lian: Størrelser og enheter i fysikk og teknikk, eller Lian og Angell: Fysiske størrelser og enheter; Aylward & Findlay: SI Chemical Data.

A formula sheet is attached .

Sensuren faller i uke 24.

<u>**Problem 1**</u> (Subproblems <u>a</u>, <u>b</u>, <u>c</u> and <u>d</u> count 5%, 7%, 7% and 7%, respectively)



A particle with mass m is moving in a one-dimensional, symmetric potential

$$V(x) = \begin{cases} V_0 & \text{for } -b < x < b, \\ 0 & \text{for } b < |x| < b + l, \\ \infty & \text{for } |x| > b + l. \end{cases}$$

Here the width l of the "wells" can be considered to be a fixed length, while the length 2b of the barrier is a variable parameter. Thus, in the limit  $b \to 0$  the potential V(x) approaches an ordinary box potential (infinite square well) of width 2l.

**<u>a.</u>** All the states of this symmetric potential are bound states. •What can you then say about the *degree of degeneracy* (i.e., the number of independent energy eigenstates for each energy eigenvalue E)? •What symmetry property and how many zeroes (nodes) does the ground state have? •Same questions for the first and second excited states. [Proofs are not required. Do not count the zeroes for  $x = \pm (b+l)$ .]

**<u>b.</u>** For a given width l of the "wells", it is possible to choose the barrier height  $V_0$  in such a way that one of the energy eigenfunctions of this potential, namely the one with two zeroes  $[x = \pm(b+l) \text{ not counted}]$ , takes the form

 $\psi(x) = C = \text{constant} \quad \text{for} \quad -b < x < b.$ 

•What can you say about the energy E of this eigenstate compared with the barrier height  $V_0$ ? [Hint: Use the time-independent Schrödinger equation.] •What are the continuity properties of this energy eigenfunction at the points  $x = \pm b$ ? •Same question for the points  $x = \pm (b + l)$ ? (Proof not required.)

**<u>c.</u>** •Make a sketch of the energy eigenfunction  $\psi(x)$ , •find the barrier height  $V_0$  and the energy E, and show that these quantities depend on l, but not on b.

**<u>d</u>.** •How many energy eigenfunctions with *lower* energy than that found above does one have for this potential? •Check the result above for the energy E by considering the limiting case  $b \to 0$ .

## <u>**Problem 2**</u> (Subproblems $\underline{a}, \underline{b}, \underline{c}$ and $\underline{d}$ each count 7%)

**<u>a.</u>** A particle with mass m is moving in a one-dimensional potential V(x). This system is in a state described by the normalised wave function

$$\Psi(x,t) = C e^{-a(mx^2/\hbar + it)}.$$

•Write down the time-dependent Schrödinger equation for this system. •Set in the given wave function and show that the potential is harmonic, that is, that it can be written as  $V(x) = \frac{1}{2}m\omega^2 x^2$ . (Find  $\omega$  expressed in terms of a.)

**<u>b.</u>** •Explain what is meant by a *stationary solution* of the time-dependent Schrödinger equation. Show that the solution given above is stationary, and find the energy E.

The expectation value of the potential energy of this state obviously is  $\langle V \rangle = \frac{1}{2}m\omega^2 \langle x^2 \rangle$ . •Use the formula

$$\langle K \rangle = \frac{1}{2m} \int \Psi^* \, \hat{p}_x^2 \, \Psi \, dx = \frac{\hbar^2}{2m} \int |\partial \Psi / \partial x|^2 dx$$

to show that also the expectation value  $\langle K \rangle$  of the *kinetic* energy can be expressed as  $\frac{1}{2}m\omega^2 \langle x^2 \rangle$  in this case. [Hint: Write  $\partial \Psi / \partial x$  as  $\Psi$  multiplied by a factor, and note that you don't need to *compute* any of the integrals.]

**c.** The state above actually is the ground state of the harmonic potential  $V(x) = \frac{1}{2}m\omega^2 x^2$ . This can be shown by several methods, one of which is the series expansion method. An alternative method is to try to minimize  $\langle K + V \rangle_{\psi}$  for an arbitrarily chosen, normalised spatial wave function  $\psi(x)$  (without worrying whether it is an energy eigenfunction or not): •Start by showing that

$$\langle V \rangle_{\psi} + \langle K \rangle_{\psi} = \frac{1}{2}m\omega^2 [(\Delta x)^2_{\psi} + \langle x \rangle^2_{\psi}] + \frac{1}{2m} [(\Delta p_x)^2_{\psi} + \langle p_x \rangle^2_{\psi}].$$

[Hint: See the definition of uncertainties on the formula sheet.] Here, in order to make the right-hand side as small as possible, we can ("without loss of generality")

(i) choose  $\psi(x)$  real,

(ii) "move" the function  $\psi(x)$  along the x axis so that  $\langle x \rangle_{\psi} = 0$ .

•Show that (i) implies that  $\langle p_x \rangle_{\psi} = 0$ .

In the resulting expression

$$\langle V \rangle_{\psi} + \langle K \rangle_{\psi} = \frac{1}{2}m\omega^2(\Delta x)_{\psi}^2 + \frac{1}{2m}(\Delta p_x)_{\psi}^2$$

it is now obvious that  $\langle V \rangle_{\psi}$  can be made arbitrarily small by choosing a function  $\psi(x)$  with sufficiently small "extension"  $(\Delta x)_{\psi}$  but, as we shall see, this is not necessarily the smartest thing to do. •Suppose that we, for a chosen value of  $(\Delta x)_{\psi}$ , choose our function  $\psi(x)$  so that  $(\Delta p_x)_{\psi}$  is as small as possible (for the chosen value of  $(\Delta x)_{\psi}$ ). State what the value of this smallest possible size of  $(\Delta p_x)_{\psi}$  is, expressed in terms of  $(\Delta x)_{\psi}$ .

**<u>d</u>.** With the choice just mentioned,  $\langle V \rangle_{\psi} + \langle K \rangle_{\psi}$  becomes a function of  $(\Delta x)_{\psi}$ . In this function it is convenient to introduce a dimensionless variable D, as follows:

$$(\Delta x)^2_{\psi} = \frac{\hbar}{2m\omega} D.$$

•Express  $\langle V + K \rangle_{\psi}$  in terms of D, and discuss the behaviour of this expression as a function of D. •What is your conclusion regarding the possibility of finding energy eigenstates with lower energy than that found in point **<u>b</u>** above (for the potential at hand)?

## <u>**Problem 3**</u> (Subproblems <u>a</u>, <u>b</u> and <u>c</u> each count 7%)

An electron is moving in the Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

By a measurement of the observables E,  $\mathbf{L}^2$  and a particular component of the angular momentum,  $\hat{\mathbf{n}} \cdot \mathbf{L}$  (where the unit vector  $\hat{\mathbf{n}}$  is unknown so far), this system is prepared in a state described by the normalised wave function

$$\psi(\mathbf{r}) = R(r) X(\theta, \phi), \quad \text{where} \quad X(\theta, \phi) = \frac{1}{2} Y_{p_x} + \frac{1}{2} \sqrt{3} Y_{p_y}.$$

According to the measurement postulate,  $\psi(\mathbf{r})$  must then be a simultaneous eigenfunction of the operators  $\hat{H}$ ,  $\hat{\mathbf{L}}^2$  and  $\hat{\mathbf{n}} \cdot \hat{\mathbf{L}}$  (which are commuting operators), and the respective eigenvalues must be identical with the values measured in the preparation of this state.

**<u>a.</u>** •What is the value for  $\mathbf{L}^2$  measured in the preparation just mentioned? (Use the formula sheet. Avoid lengthy calculations.)

The function  $Y_{p_z} = \sqrt{3/4\pi} \,\hat{\mathbf{z}} \cdot \mathbf{r}/r$  obviously is rotationally symmetric around the z axis. The function  $X(\theta, \phi)$  has the same form seen from another axis, which we can call  $\hat{\mathbf{n}}$ . •Find this unit vector  $\hat{\mathbf{n}}$  (and state in what direction it points) by writing  $X(\theta, \phi)$  on the form

$$X(\theta,\phi) = \sqrt{\frac{3}{4\pi}} \,\frac{\hat{\mathbf{n}} \cdot \mathbf{r}}{r} = \sqrt{\frac{3}{4\pi}} \,\frac{n_x x + n_y y + n_z z}{r}.$$

**<u>b.</u>** The fact that  $Y_{p_z}$  and X have the same form (seen from the  $\hat{\mathbf{z}}$  and  $\hat{\mathbf{n}}$  axes, respectively) means that

$$\hat{\mathbf{n}} \cdot \hat{\mathbf{L}} X(\theta, \phi) = 0,$$

in analogy with  $\hat{\mathbf{z}} \cdot \hat{\mathbf{L}} Y_{p_z} = \hat{L}_z Y_{p_z} = 0$ . This means that  $\hat{\mathbf{n}} \cdot \mathbf{L}$  was measured to zero in the preparation of the state  $\psi(\mathbf{r}) = R(r)X(\theta, \phi)$ .

Suppose now that a *new measurement* is made on this system, this time of the observable  $L_z$ , after the preparation of the state  $\psi(\mathbf{r})$  by the first measurement. •State what the possible measured values for  $L_z$  are in the new measurement, and find the corresponding probabilities. [Hint: Express X and hence  $\psi$  in terms of spherical harmonics  $Y_{lm}$ .] •Why must such a new measurement necessarily *change the state* of the system?

 $\underline{\mathbf{c.}}$  The energy eigenvalues of the bound states of the present system can in general be written as

$$E_n = -\frac{1}{2} (\alpha Z)^2 \frac{m_e c^2}{n^2}$$
, where  $n = l + 1 + n_r$ .

Here,  $n_r$  is the so-called *radial quantum number*. The figure shows the radial density  $[rR(r)]^2$  for the given state  $\psi(\mathbf{r})$ , as a function of  $r/a = Zr/a_0$ .



•Explain what the radial quantum number  $n_r$  stands for, and state its value for the prepared state  $\psi(\mathbf{r}) = R(r)X(\theta, \phi)$ . State the value of the principal quantum number n for this state.

•What values can the angular-momentum quantum number l take in general for the system at hand (including the *l*-value found in point <u>a</u> above), for the present value of n? How many independent spatial energy eigenfunctions does this system have for the present value of n?

**Problem 4** (Subproblems 4a, 4b, and 4c count 4%, 8%, and 5%, respectively.) Acetylene, or ethyne, has chemical formula  $C_2H_2$ . The molecule is linear, with a triple bond between the two carbon atoms:



The geometry of the molecule is determined by the two bond lengths C-C and C-H, which in a Hartree–Fock calculation with the basis set 3-21G(\*) [i.e., two *s*-orbitals per H-atom and three *s*- and six *p*-orbitals per C-atom] is 1.188 and 1.051 Å, respectively. We assume that the four atomic nuclei lie on the *z*-axis, and that the symmetry centre of the molecule coincides with the origin.

<u>**a.**</u> How many electrons are there all together in the acetylene molecule? In the LCAO approximation, the single particle states (molecular orbitals, "MOs")  $\Psi_i$  of the molecule are written as linear combinations of atomic orbitals (basis functions)  $\phi_{\mu}$ :

$$\Psi_i = \sum_{\mu=1}^M c_{\mu i} \phi_\mu$$

The coefficients  $c_{\mu i}$  denote to what extent a given basis function (e.g. the 1*s*-orbital  $\phi_{1s}$  on one of the H-atoms) contributes to MO number *i*. How many basis functions *M* contribute to this sum in acetylene, with the chosen basis set 3–21G(\*)? How many MOs are occupied by electrons in acetylene? (Remember the Pauli principle, in addition to the fact that each MO represents two single particle states, since an electron may have spin "up" or spin "down". We consider the ground state only.)

**<u>b.</u>** The triple bond between the two C–atoms is made up of six of the electrons in the molecule. These electrons occupy, among others, MO number 3 and MO number 7:



Here, the MOs are numbered such that higher numbers correspond to higher energies. Light grey denotes a surface with a constant positive value of the MO, dark grey denotes a surface with the corresponding negative value of the MO. Coordinates are chosen such that the x-axis points into the plane, the y-axis upwards, and the z-axis to the right. What is the parity of the two MOs  $\Psi_3$  and  $\Psi_7$  (i.e.: even or odd)?

One of these two is a so-called  $\sigma$ -orbital, consisting of *s*-orbitals on all four atoms in addition to  $p_z$ -orbitals on the carbon atoms, the other MO is a so-called  $\pi$ -orbital. Which of the two is a  $\sigma$ -orbital and which is a  $\pi$ -orbital? What kind of basis functions contribute to this  $\pi$ -orbital? MO number 6 also contributes to the triple bond between the carbon atoms. This orbital has exactly the same energy as MO number 7. Use this information, together with the symmetry of the molecule, to determine what kind of basis functions that contribute to  $\Psi_6$ .

Four of the electrons in acetylene do not really contribute much to the chemical bonds between the atoms in the molecule. These electrons occupy the MOs that are illustrated in the figure below:



These two MOs are, respectively, an antisymmetric and a symmetric linear combination of the same atomic orbitals. Which atomic orbitals? Which one of these two MOs has the lower energy? Provide a reason for your answer. What can you say about the energy of these two MOs, in comparison with, e.g., the energy of  $\Psi_7$ ? (Note: In the figure illustrating  $\Psi_3$  and  $\Psi_7$ , the value of the MOs is (±) 0.032; in the last figure, the value of the MOs is (±) 0.010.)

<u>c.</u> Acetylene has seven vibrational modes. The figure below illustrates four of these. The arrows denote the direction of the displacement of the four atoms in the molecule for each vibrational movement. Corresponding wave numbers k are given in the unit cm<sup>-1</sup>. Which of these vibrational modes are so-called IR-active? (A vibrational mode is IR-active if the corresponding vibrational movement represents an oscillating electric dipole.) Your friend, the chemist, talks about "C–C stretch" and "C–H stretch" when you discuss the vibrational modes in acetylene. Which of the four modes in the figure below is she then referring to?



## Problem 5 (Counts 8%)

With a good catalyst, alkenes like ethene  $(C_2H_4)$  and propene  $(C_3H_6)$  may be polymerized to polyethene and polypropene, respectively, at relatively low temperatures, in fact down to zero degrees centigrades. This implies that the activation energy  $E_a$  for each "insertion reaction"

$$P_n + A \to P_{n+1}$$

is quite small. Here,  $P_n$  denotes a polymer chain with n monomers whereas A denotes an alkene.

We may model this reaction with the energy function

$$E(x) = E_0 \left(\frac{5x^4}{8} - 2x^3 + x^2\right)$$

where x represents a (dimensionless) reaction coordinate and  $E_0 = 10$  kcal/mol. We assume that the reaction starts in the local minimum  $x_i = 0$ , proceeds in the direction of increasing x via a transition state (local maximum) at  $x_{\text{TS}}$ , and ends up in an energy minimum at  $x_f$ . Determine  $x_{\text{TS}}$  and  $x_f$ , and subsequently the activation energy of the reaction,  $E_a = E_{\text{TS}} - E_i$ . Also determine the polymerization energy  $\Delta E = E_f - E_i$ . Verify that the three stationary points are minima, alternatively maxima. (Hint: Consider the second derivative of E.)



Appendix:

Formulae and expressions (Some of these formulae may be useful.) Uncertainty

$$\begin{split} (\Delta A)^2 &= \left\langle (A - \langle A \rangle)^2 \right\rangle = \left\langle A^2 \right\rangle - \langle A \rangle^2; \qquad \Delta A \cdot \Delta B \geq \frac{1}{2} \left| \left\langle i[\hat{A}, \hat{B}] \right\rangle \right|; \\ \Delta x \cdot \Delta p_x \geq \frac{1}{2} \hbar. \end{split}$$

the Laplace operator and the angular-momentum operators in spherical coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2};$$
$$\hat{\mathbf{L}}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \qquad \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi};$$
$$\hat{L}_x = \frac{\hbar}{i} \left( -\sin\phi \frac{\partial}{\partial \theta} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right), \qquad \hat{L}_y = \frac{\hbar}{i} \left( \cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right);$$
$$[\hat{\mathbf{L}}^2, \hat{L}_z] = 0, \qquad [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad \text{etc.}$$

Spherical harmonics and other angular functions

$$\begin{cases} \hat{\mathbf{L}}^{2} \\ \hat{L}_{z} \end{cases} Y_{lm} = \begin{cases} \hbar^{2}l(l+1) \\ \hbar m \end{cases} Y_{lm}, \quad l = 0, 1, 2, ...; \qquad \int_{0}^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) Y_{l'm'}^{*} Y_{lm} = \delta_{l'l} \delta_{m'm}; \\ Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \equiv Y_{p_{z}}, \qquad Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}; \\ Y_{p_{x}} = \sqrt{\frac{3}{4\pi}} \frac{x}{r} = \frac{1}{\sqrt{2}} (Y_{1,-1} - Y_{11}), \qquad Y_{p_{y}} = \sqrt{\frac{3}{4\pi}} \frac{y}{r} = \frac{i}{\sqrt{2}} (Y_{11} + Y_{1,-1}). \end{cases}$$

Some constants

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529 \cdot 10^{-10} \text{ m} \quad \text{(Bohr radius)};$$
$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.0360} \quad \text{(fine structure constant)};$$
$$\frac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6 \text{ eV} \quad \text{(Rydberg energy)}.$$