NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET Institutt for fysikk

Faglig kontakt under eksamen: Ingjald Øverbø, tel. 73 59 18 67, eller 97 01 23 55 Jon Andreas Støvneng, tel. 73 59 36 63, eller 45 45 55 33

EKSAMEN I TFY4215 KJEMISK FYSIKK OG KVANTEMEKANIKK

Lørdag 16. august 2008 kl. 9.00 - 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.

Sheets with formulae and expressions (attachment 1) and chemical naming rules (attachment 2) are attached.

Sensuren faller i august 2008.

Question 1 (Counts 34 %)



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

 $V(x) = \begin{cases} \infty & \text{for} & |x| > a, \\ V_0 & \text{for} & a/2 < |x| < a, \\ 0 & \text{for} & -a/2 < x < a/2. \end{cases}$

In this Problem the parameter a is kept fixed, while V_0 is a parameter that can be varied, from large negative values towards $+\infty$.



The figure shows a sketch of the ground-state energy E_1 as a function of V_0 . It turns out that E_1 is a monotonically increasing function of V_0 , as are all the other energy eigenvalues.

<u>a.</u> Suppose that V_0 is finite. •State without proof the number of zeros in the interval -a < x < a — and describe the symmetry properties — for the ground state ψ_1 and the first excited state ψ_2 . •Which conditions must be satisfied by *all* energy eigenfunctions ψ_n for the potential V(x) in the points $x = \pm a$ and $x = \pm a/2$? For the special case $V_0 = 0$, all the energy eigenfunctions are sinusoidal for |x| < a; $\psi_n = A_n \sin[k_n(x-a)]$. •Sketch the ground state ψ_1 and the first excited state ψ_2 for $V_0 = 0$.

b. •Determine the wave numbers k_1 and k_2 for the ground state and the first excited state for the special case $V_0 = 0$. •Check that the resulting solutions ψ_1 and ψ_2 satisfy the timeindependent Schrödinger equation, and find the energies $E_1(0)$ and $E_2(0)$, for the special case $V_0 = 0$. •What are the energies $(E_1(\infty) \text{ and } E_2(\infty))$ when V_0 is infinitely high?

<u>c.</u> For a certain negative value of V_0 ($V_0 = V_a < 0$), the ground-state energy E_1 is equal to zero (cf the diagram above).



•Use (among other things) the time-independent Schrödinger equation to find the form of the ground state ψ_1 in the region -a/2 < x < a/2 in this case. •Sketch ψ_1 for all x. •Determine (the negative) potential value V_a , based on the sketch and the time-independent Schrödinger equation.

<u>**d.**</u> For a certain *positive* value of V_0 ($V_0 = V_b > 0$), the ground state energy is equal to V_0 (see the diagram at the top of the preceding page).



Make a sketch of the ground state ψ_1 for this case. For this case, we may write

$$V_b = E_1 = \frac{\hbar^2 k_b^2}{2m}.$$

•Find a condition that determines the wave number k_b . •Make a rough estimate of the wave number k_b based on the sketch. •Find an accurate value for k_b and hence for the potential value V_b , expressed in terms of a.

Question 2 (Counts 25 %)

A particle with mass m is moving in the one-dimensional harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$. The ground state of this system is

$$\psi_g = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar},$$

with the energy $E_g = \frac{1}{2}\hbar\omega$.

<u>a.</u> •Use the formula

$$\langle K \rangle_{\psi} = \left\langle \frac{p_x^2}{2m} \right\rangle_{\psi} = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{\partial \psi}{\partial x} \right|^2 dx$$

to show that the expectation value of the kinetic energy in the ground state may be written on the form

$$\langle K \rangle_g = \frac{1}{2} m \omega^2 \left\langle x^2 \right\rangle_g$$

which means that it is equal to the expectation value $\langle V \rangle_g$ of the *potential* energy. [Hint: Use that $\partial \psi_g / \partial x = (-m\omega x/\hbar)\psi_g$.] •What is $\langle K + V \rangle_g$ for the ground state? •Use this to find $\langle x^2 \rangle_g$ and $\langle p_x^2 \rangle_g$ for the ground state. •Find also the expectation values $\langle x \rangle_g$ and $\langle p_x \rangle_g$ for the ground state, and determine the uncertainties $(\Delta x)_g$ and $(\Delta p_x)_g$, together with the uncertainty product $(\Delta x)_g (\Delta p_x)_g$. **<u>b.</u>** Suppose that this system is at t = 0 prepared in (the normalized) initial state

$$\Psi(x,0) = \sqrt{10} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-100m\omega x^2/2\hbar} \equiv \psi_b(x)$$

which is strongly "squeezed" compared to the ground state (see the figure).



For $t \ge 0$, the wave function of this system may be expanded in terms of the set of stationary states of the oscillator (see the formula sheet):

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}; \qquad c_n = \langle \psi_n, \Psi(0) \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \Psi(x,0) dx.$$

•What is the physical interpretation of the coefficients c_n ? •Why is c_n equal to zero for $n = 1, 3, 5, \dots$? •Which symmetry property for $\Psi(x, t)$ follows from this?

As a function of t, the wave function $\Psi(x,t)$ will vary strongly in form and extension but, after one half of the classical period, $T/2 = \pi/\omega$, the probability density is in fact unchanged. •Show this. [Hint: Start by finding the constant f in the relations

$$\exp[-iE_n(t+T/2)/\hbar] = f \cdot \exp[-iE_nt/\hbar] \qquad (n = 0, 2, 4, \cdots),$$

and use this to find the relation between $\Psi(x, t + T/2)$ and $\Psi(x, t)$.]

<u>c.</u> As a consequence of the squeezing of the initial state, the expectation value $\langle V \rangle_b$ of the potential energy is a factor 100 less than in the ground state. Thus, at t = 0 the particle is located at the origin, roughly speaking. For the same reason the expectation value $\langle K \rangle_b$ of the kinetic energy is a factor 100 *larger* than in the ground state, so that the particle is fairly "energetic". •You are now invited to speculate in a qualitative way about what happens with the probability distribution *between* the times when it is recreated, i.e., between the times t = 0, T/2, T, 3T/2 etc. •Try also to make a semiclassical estimate of the average squared distance from the origin (and hence of the uncertainty Δx) when these quantities are on their largest. [Hint: How far out does the particle move classically if it has an energy E? And what is $\langle E \rangle$ in the state $\Psi(x, t)$?]

Question 3 (Counts 16 %)

<u>a</u>. For a particle with mass m in the one-dimensional harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$, the eigenfunctions $\psi_n(x)$ given on the formula sheet are the only solutions of the energy eigenvalue equation which go to zero when $x \to \pm \infty$.



•Based on this, state the results for the wave functions and the energies of the ground state and the first excited state when the particle is moving in the one-dimensional potential

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2 x^2 & \text{for} \quad x > 0, \\ \infty & \text{for} \quad x < 0. \end{cases}$$

b. An electron is moving in the three-dimensional potential

$$V = \begin{cases} -\frac{e^2}{4\pi\epsilon_0 r} & \text{for } z > 0, \\ \infty & \text{for } z < 0. \end{cases}$$

•Find, using the known energy eigenfunctions for hydrogenlike systems, the ground-state wave function for this system and the corresponding energy. •What is the energy and the (degree of) degeneracy for the first excited level?

Question 4 (Counts 10%)

Give short answers to these four questions:

• In quantum mechanical calculations on atoms and molecules, one usually applies the socalled Born – Oppenheimer – approximation. What does that mean?

• What is contained in the Pauli principle?

• A (non-linear) molecule with N atoms has 3N (spatial) degrees of freedom. How many of these are associated with translation of the molecule, rotation of the molecule, and vibrations within the molecule?

• Draw and give name to the three different isomers of dibromo-ethene.

Question 5 (Counts 15%)

A chemical equilibrium reaction

$$A \rightleftharpoons B$$

is described by the following energy function E(x):



Here, E is the total energy of the system, and the reaction coordinate x may (for example) be the relative deviation from the equilibrium value R_0 of a certain interatomic distance in the system, i.e., $x = (R - R_0)/R_0$.

• Discuss how the kinetics and the thermodynamic equilibrium between the two states A and B depend on the various energies given in the figure above.

We may model such a chemical equilibrium with the energy function

$$E(x) = E_0 \left(\frac{35x^4}{8} - 2x^3 + \frac{x^2}{4}\right)$$

where $E_0 = 343$ eV.

• Determine x_A, x_{TS} and x_B . Verify that x_{TS} corresponds to a (local) energy maximum. (Hint: Consider the second derivative of E.)

Assume that A and B are different conformations of the same molecule (i.e., B may be obtained from A, and vice versa, by e.g. a rotation around one of the chemical bonds in the system).

• Determine the ratio N_A/N_B between the number of molecules in state A and state B in such a gas in thermodynamic equilibrium at room temperature (T = 300 K). Will this ratio become smaller or larger if the temperature is decreased? Give a brief explanation for your answer.

Given: Boltzmann's constant $k_B = 8.617 \cdot 10^{-5} \text{ eV/K}.$

Attachment 1: Formulae and expressions (Some of this may turn out to be useful.)

One-dimensional harmonic oscillator

$$\begin{pmatrix} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \end{pmatrix} \psi_n(x) = \hbar\omega(n + \frac{1}{2})\psi_n(x); \qquad \langle \psi_n, \psi_k \rangle = \delta_{nk}; \\ \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-y^2/2} H_n(y), \qquad y = \frac{x}{\sqrt{\hbar/m\omega}}; \\ H_0(y) = 1, \quad H_1(y) = 2y, \quad H_2(y) = 4y^2 - 2, \quad H_3(y) = 8y^3 - 12y, \quad \cdots; \\ \widehat{\mathcal{P}}\psi_n(x) \equiv \psi_n(-x) = (-1)^n \psi_n(x).$$

The Laplace operator and angular-momentum operators in polar coordinates

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

Angular functions

$$\begin{cases} \hat{\mathbf{L}}^{2} \\ \hat{L}_{z} \end{cases} Y_{lm} = \begin{cases} \hbar^{2} l(l+1) \\ \hbar m \end{cases} Y_{lm}, \quad l = 0, 1, 2, ...; \qquad \int_{0}^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) Y_{l'm'}^{*} Y_{lm} = \delta_{l'l} \delta_{m'm}; \\ Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \equiv Y_{p_{z}}, \qquad Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}; \\ Y_{p_{x}} = \sqrt{\frac{3}{4\pi}} \frac{x}{r} = \frac{1}{\sqrt{2}} (Y_{1,-1} - Y_{11}), \qquad Y_{p_{y}} = \sqrt{\frac{3}{4\pi}} \frac{y}{r} = \frac{i}{\sqrt{2}} (Y_{11} + Y_{1,-1}); \\ Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^{2}\theta - 1); \qquad Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi}; \qquad Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^{2}\theta e^{\pm 2i\phi}. \\ \widehat{\mathcal{P}}Y_{lm} = (-1)^{l}Y_{lm}. \end{cases}$$

Energy eigenfunctions and radial equation, spherically symmetric potential V(r)

$$\psi(r,\theta,\phi) = \frac{u(r)}{r} Y_{lm}(\theta,\phi);$$
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}}^l(r)\right] u(r) = E u(r), \qquad V_{\text{eff}}^l(r) \equiv V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \qquad u(0) = 0.$$

Energy eigenfunctions and eigenvalues, hydrogenlike system, $V(r) = -Ze^2/(4\pi\epsilon_0 r)$

$$E_n = \frac{E_1}{n^2} \equiv \frac{E_1}{(l+1+n_r)^2}, \qquad E_1 = -\frac{1}{2} (\alpha Z)^2 m_e c^2;$$

$$\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi);$$

$$R_{10} = \frac{2}{a^{3/2}} e^{-r/a}; \qquad R_{20} = \frac{1}{\sqrt{2} a^{3/2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}; \qquad R_{21} = \frac{1}{2\sqrt{6} a^{3/2}} \frac{r}{a} e^{-r/2a}; \qquad a = \frac{a_0}{Z}.$$

Some constants

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529 \cdot 10^{-10} \text{ m} \qquad \text{(Bohr-radien)};$$
$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.0360} \qquad \text{(finstrukturkonstanten)};$$
$$\frac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6 \text{ eV} \qquad \text{(Rydberg-energien)}.$$

Some formulae

$$\sin a = (e^{ia} - e^{-ia})/2i, \qquad \cos a = (e^{ia} + e^{-ia})/2;
\tan y = \frac{1}{\cot y} = \tan(y + n\pi), \qquad n = 0, \pm 1, \cdots;
\sinh y = \frac{1}{2}(e^y - e^{-y}); \qquad \cosh y = \frac{1}{2}(e^y + e^{-y}); \qquad \tanh y = \frac{1}{\coth y} = \frac{\sinh y}{\cosh y};
\cosh^2 y - \sinh^2 y = 1; \qquad \frac{d}{dy} \sinh y = \cosh y; \qquad \frac{d}{dy} \cosh y = \sinh y.$$

Attachment 2. Naming rules in organic chemistry.

Rank	Main group	Function	al group	Prefix	Suffix
1	Carboxylic acid	-COOH		(carboxy-)	-oic acid
2	Carboxylic acid anhydride	-СО-О-СО-	$-\mathbf{C} - \mathbf{O} - \mathbf{C} - \mathbf{O}$		-oic anhydride
3	Ester †	-COOR	$-\mathbf{C} - \mathbf{O} - \mathbf{R}$		-oate
4	Carboxylic acid halide †	-COX	$-\mathbf{C} - \mathbf{X}$	halocarbonyl-	-oyl halide
5	Amide	-CONH ₂	$- \overset{ }{\mathbf{C}} - \mathrm{NH}_2$	amido-	-amide
6	Nitrile	-CN	$-C \equiv N$	cyano-	-nitrile
7	Aldehyde	-COH	$-\overset{\mathrm{O}}{\mathrm{C}}-\mathrm{H}$	OXO-	-al
8	Ketone	-CO-	$-\mathbf{c}^{ }$	OXO-	-one
9	Alcohol	-O	Н	hydroxy-	-ol
10	Thiol	-S]	H	mercapto-	-thiol
11	Amine	-NI	H_2	amino-	-amine
12	Imine	>C=	=N-	imino-	-imine
13	Alkene	-C=	-C-		-ene
14	Alkyne	-C≡	EC-		-yne
15	Alkane	-C-	С-		-ane

Table 1: Some functional groups, ranked according to decreasing priority

Secondary groups (no priority)	Functional group	Prefix	Suffix
Ether	-С-О-С-	alkoxy-	-ether
Halide †	-X	halo- (e.g. chloro-)	
Nitro	$-NO_2$	nitro-	

 $\dagger X = a$ halogen (F, Cl, Br, or I), R = (usually) an alkyl group $(C_n H_{2n+1})$

Naming organic compounds:

[Prefix(es) including numbering] - [Main skeleton] - [Suffix]

- Suffix: functional group with highest rank
- Main skeleton: longest connected carbon chain, numbered so that the suffix group sits on the lowest possible number
- Prefix(es) incl numbering: all substituents on the main skeleton, in alphabetical order