

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

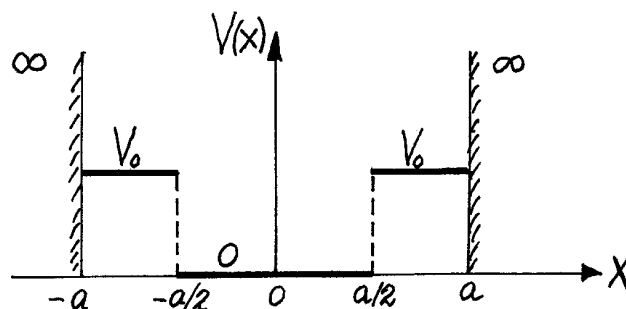
kl. 9.00 - 13.00

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.

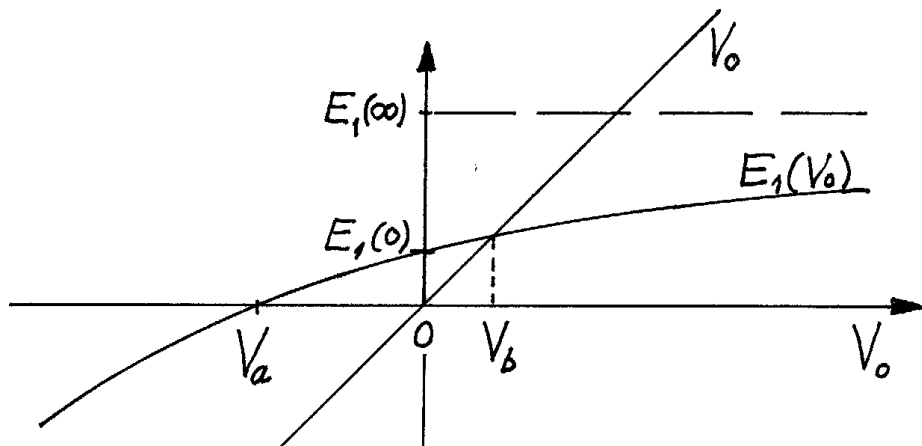
### Question 1 (Counts 34 %)



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  $+\infty$ .

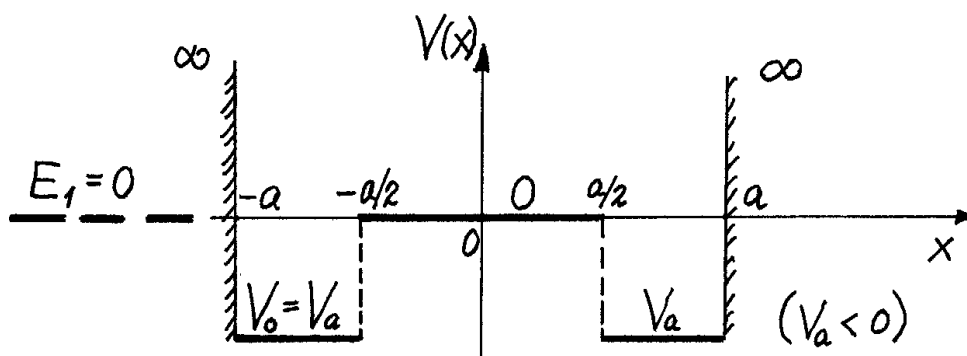


The figure shows a sketch of the ground-state energy  $E_1$  as a function of  $V_0$ . It turns out that  $E_1$  is a monotonically increasing function of  $V_0$ , as are all the other energy eigenvalues.

**a.** 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  $\psi_1$  and the first excited state  $\psi_2$ . •Which conditions must be satisfied by *all* energy eigenfunctions  $\psi_n$  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  $\psi_1$  and the first excited state  $\psi_2$  for  $V_0 = 0$ .

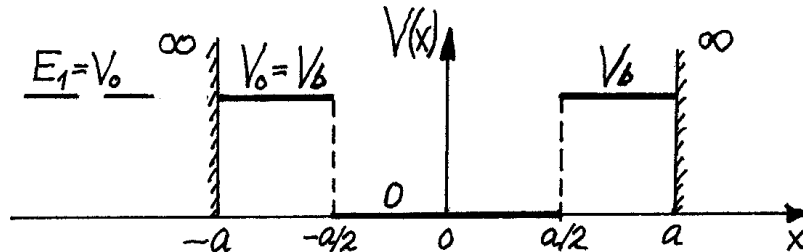
**b.** •Determine the wave numbers  $k_1$  and  $k_2$  for the ground state and the first excited state for the special case  $V_0 = 0$ . •Check that the resulting solutions  $\psi_1$  and  $\psi_2$  satisfy the time-independent Schrödinger equation, and find the energies  $E_1(0)$  and  $E_2(0)$ , for the special case  $V_0 = 0$ . •What are the energies ( $E_1(\infty)$  and  $E_2(\infty)$ ) when  $V_0$  is infinitely high?

**c.** 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  $\psi_1$  in the region  $-a/2 < x < a/2$  in this case. •Sketch  $\psi_1$  for all  $x$ . •Determine (the negative) potential value  $V_a$ , based on the sketch and the time-independent Schrödinger equation.

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



Make a sketch of the ground state  $\psi_1$  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 masse  $m$  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  $E_g = \frac{1}{2}\hbar\omega$ .

**a.** •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

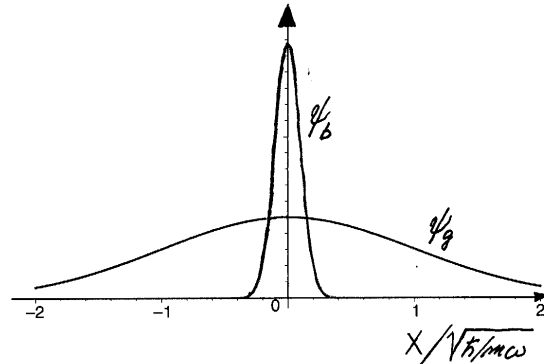
$$\langle K \rangle_g = \frac{1}{2}m\omega^2 \langle x^2 \rangle_g,$$

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 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  $(\Delta x)_g(\Delta p_x)_g$ .

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

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

•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

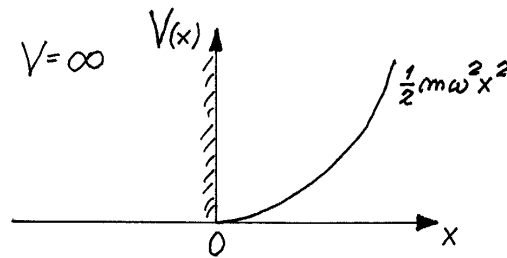
$$\exp[-iE_n(t + T/2)/\hbar] = f \cdot \exp[-iE_n t/\hbar] \quad (n = 0, 2, 4, \dots),$$

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

**c.** As a consequence of the she 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  $\Delta x$ ) 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 %)

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

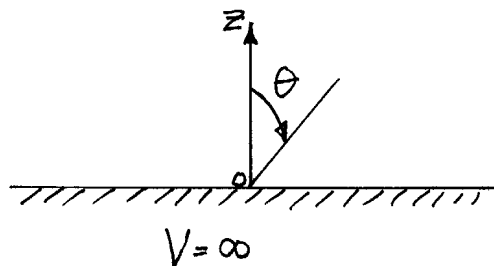


•Base on this, state the results for the wave functions and the energies of the ground state and the first excited state when the particle is moving in the one-dimensional potential

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

**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?

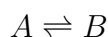
**Oppgave 4** (Teller 10%)

Svar kort på disse fire spørsmålene:

- I kvantemekaniske beregninger på atomer og molekyler benyttes som regel den såkalte Born – Oppenheimer – approksimasjonen. Hva innebærer det?
- Hva uttrykker Pauliprinsippet?
- Et (ikke-lineært) molekyl med  $N$  atomer har  $3N$  (romlige) frihetsgrader. Hvor mange av disse er knyttet til henholdsvis translasjon av molekylet, rotasjon av molekylet, og vibrasjoner i molekylet?
- Tegn opp og navngi de tre ulike isomere av dibrometen.

**Oppgave 5** (Teller 15%)

En kjemisk likevekt



beskrives av følgende energifunksjon  $E(x)$ :

Her er  $E$  systemets totale energi, og reaksjonskoordinaten  $x$  kan (f.eks) være det relative avvik fra likevektsverdien  $R_0$  til en bestemt interatomær avstand i systemet, dvs  $x = (R - R_0)/R_0$ .

- Diskuter hvordan kinetikken og den termodynamiske likevekten mellom de to tilstandene  $A$  og  $B$  avhenger av de ulike energiene angitt i figuren.

Vi kan modellere en slik kjemisk likevekt med energifunksjonen

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

der  $E_0 = 343$  eV.

- Bestem  $x_A$ ,  $x_{TS}$  og  $x_B$ . Verifiser at  $x_{TS}$  tilsvarer et (lokalt) energimaksimum. (Tips: Betrakt den andrederiverte av  $E$ .)

Anta at  $A$  og  $B$  er ulike konformasjoner av samme molekyl (dvs at  $B$  kan oppnås fra  $A$ , og omvendt, ved f.eks dreining omkring en av systemets kjemiske bindinger).

- Bestem forholdet  $N_A/N_B$  mellom antall molekyler i tilstand  $A$  og tilstand  $B$  i en slik gass i termodynamisk likevekt ved romtemperatur ( $T = 300$  K). Vil dette forholdet bli mindre eller større dersom temperaturen senkes? Begrunn svaret kort.

Oppgitt: Boltzmanns konstant  $k_B = 8.617 \cdot 10^{-5}$  eV/K.

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

**One-dimensional harmonic oscillator**

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right) \psi_n(x) = \hbar\omega\left(n + \frac{1}{2}\right)\psi_n(x); \quad \langle \psi_n, \psi_k \rangle = \delta_{nk};$$

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-y^2/2} H_n(y), \quad y = \frac{x}{\sqrt{\hbar/m\omega}};$$

$$H_0(y) = 1, \quad H_1(y) = 2y, \quad H_2(y) = 4y^2 - 2, \quad H_3(y) = 8y^3 - 12y, \quad \dots;$$

$$\hat{\mathcal{P}}\psi_n(x) \equiv \psi_n(-x) = (-1)^n \psi_n(x).$$

**The Laplace operator and angular-momentum operators in polar coordinates**

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{\mathbf{L}}^2}{\hbar^2 r^2};$$

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \quad \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi};$$

$$\hat{L}_x = \frac{\hbar}{i} \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \quad \hat{L}_y = \frac{\hbar}{i} \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right);$$

$$[\hat{\mathbf{L}}^2, \hat{L}_z] = 0, \quad [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, \quad \text{osv.}$$

**Angular functions**

$$\left\{ \begin{array}{l} \hat{\mathbf{L}}^2 \\ \hat{L}_z \end{array} \right\} Y_{lm} = \left\{ \begin{array}{l} \hbar^2 l(l+1) \\ \hbar m \end{array} \right\} Y_{lm}, \quad l = 0, 1, 2, \dots; \quad \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) Y_{l'm'}^* Y_{lm} = \delta_{l'l} \delta_{m'm};$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \equiv Y_{p_z}, \quad Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi};$$

$$Y_{p_x} = \sqrt{\frac{3}{4\pi}} \frac{x}{r} = \frac{1}{\sqrt{2}} (Y_{1,-1} - Y_{11}), \quad Y_{p_y} = \sqrt{\frac{3}{4\pi}} \frac{y}{r} = \frac{i}{\sqrt{2}} (Y_{11} + Y_{1,-1});$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1); \quad Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}; \quad Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}.$$

$$\hat{\mathcal{P}}Y_{lm} = (-1)^l Y_{lm}.$$

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

$$\psi(r, \theta, \phi) = \frac{u(r)}{r} Y_{lm}(\theta, \phi);$$

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

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

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

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

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

**Some constants**

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.529 \cdot 10^{-10} \text{ m} \quad (\text{Bohr-radien});$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137.0360} \quad (\text{finstrukturkonstanten});$$

$$\frac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6 \text{ eV} \quad (\text{Rydberg-energien}).$$

**Some formulae**

$$\sin a = (e^{ia} - e^{-ia})/2i, \quad \cos a = (e^{ia} + e^{-ia})/2;$$

$$\tan y = \frac{1}{\cot y} = \tan(y + n\pi), \quad n = 0, \pm 1, \dots;$$

$$\sinh y = \frac{1}{2}(e^y - e^{-y}); \quad \cosh y = \frac{1}{2}(e^y + e^{-y}); \quad \tanh y = \frac{1}{\coth y} = \frac{\sinh y}{\cosh y};$$

$$\cosh^2 y - \sinh^2 y = 1; \quad \frac{d}{dy} \sinh y = \cosh y; \quad \frac{d}{dy} \cosh y = \sinh y.$$