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

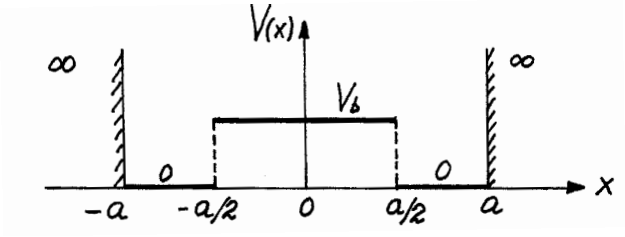
mandag 26. mai 2008
kl. 9.00 - 13.00

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.

A sheet with some formulae and expressions (attachment 1) and chemical naming rules (attachment 2) is supplied.

Sensuren faller i uke 25.

Question 1 **(Counts 33 %)**



A particle with mass m is moving in a one-dimensional box potential with a barrier in the middle,

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

In this problem the parameter a is kept fixed, while we think of V_b as a variable barrier height (or as the depth of a well if $V_b < 0$). We want to study the behaviour of the energy eigenfunctions (mostly the ground state and the first excited state), for varying values of V_b.

a. Consider first the special case $V_b = 0$. •Explain (using among other things the time-independent Schrödinger equation) why all the energy eigenfunctions can be written on the form $\psi = A\sin[k(x+a)]$ inside the box. •Determine the wave numbers k_1 and k_2 and the energies E_1 and E_2 for the ground state ψ_1 and the first excited state ψ_2, respectively.

b. •Sketch the ground state ψ_1 and the first excited state ψ_2 for the special case $V_b = 0$. •Which of the properties of ψ_1 and ψ_2 are valid for all finite values of V_b?

c. Then suppose that V_b is positive and *very large* compared with the energies found in pkt. **a**. •Make sketches of ψ_1 and ψ_2 for such a case. •Use the sketches to deduce an upper bound $E_2^{\max}$ for E_2 (so that $E_2 < E_2^{\max}$ for all V_b). [Hint: When V_b is very large, it becomes difficult to "penetrate" the barrier.] •What happens with E_1 and E_2 when V_b approaches infinity?

d. •Make sketches of ψ_1 and ψ_2 also for the case when V_b has a large negative value (deep well inside the box). •Use the sketches to find approximate results for E_1 and E_2 for such a case.

Question 2 **(Counts 42 %)**

As a simplified model of a hydrogenlike atom we consider an electron moving in the Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0\, r} = -\frac{Z\hbar^2}{m_e a_0 r}.$$

a. The ground state of this system is described by a wave function on the form

$$\psi_1 = \frac{u(r)}{r}\sqrt{\frac{1}{4\pi}}; \qquad u(r) = C\, r\, e^{-r/a}.$$

•What is the angular momentum of this state? •What do we mean by saying that this state is not excited radially? •Find the quantity a and determine the energy eigenvalue (E_1) by setting in $u(r)$ in the radial equation (given on the formula sheet).

b. For the first excited energy level, we can choose to use the four orbitals ψ_{2s}, ψ_{2p_x}, ψ_{2p_y} and ψ_{2p_z}, with

$$\begin{aligned}
\psi_{2s} &= R_{20}(r)Y_{00} = (32\pi a^3)^{-1/2}\,(\frac{r}{a} - 2)\, e^{-r/2a}, \\
\psi_{2p_z} &= R_{21}(r)Y_{p_z} = (32\pi a^3)^{-1/2}\,\frac{r}{a}\, e^{-r/2a}\,\hat{\mathbf{z}}\cdot\hat{\mathbf{r}},
\end{aligned}$$

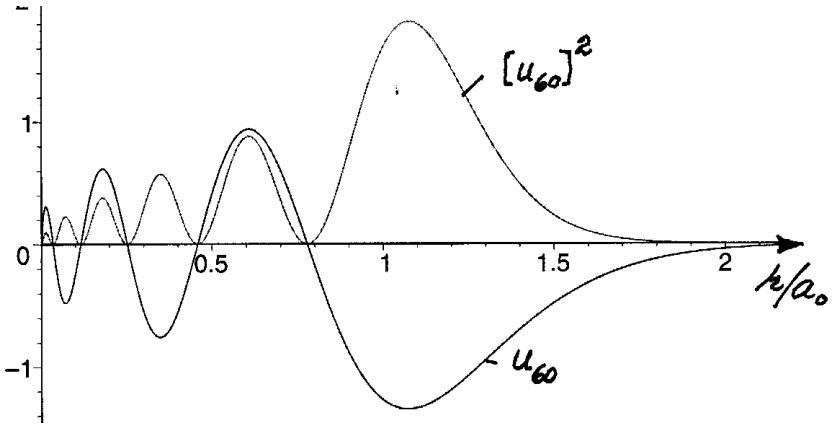
and with corresponding formulae for Y_{2p_x} and Y_{2p_y}. •Explain why the expectation value $\langle\, \mathbf{r}\,\rangle$ ("center of gravity") of the probability distribution lies at the origin for all these four orbitals. The wave function ψ_{2p_z} is rotationally symmetric with respect to an axis and antisymmetric with respect to a plane. •Which axis and which plane? •Show explicitly that ψ_{2p_x} and ψ_{2p_z} are orthogonal. •Why can we state (*without* explicit calculations) that ψ_{2s} and ψ_{2p_z} are orthogonal?

c. Instead of ψ_{2s} and ψ_{2p_z} just as well use the two linear combinations

$$\psi_\pm = c\psi_{2s} \pm \sqrt{1-c^2}\,\psi_{2p_z}$$

as energy eigenfunctions (with $0 < c < 1$). The expectation values $\langle\, \mathbf{r} \,\rangle_\pm$ of the two probability distributions $|\psi_\pm|^2$ lie on a straight line. •State and explain which line this is. The two orbitals $\psi_\pm$ are asymmetric and have a "direction", in the sense that "centers of gravity" $\langle\, \mathbf{r} \,\rangle_\pm$ lie outside the origin. •Find the distances from the origin to the points $\langle\, \mathbf{r} \,\rangle_\pm$, expressed in terms of the integral $\langle\, \psi_{2s}, z\,\psi_{2p_z} \,\rangle$, which is different from zero. •Show that these distances are maximal for the same value of the coefficient c which makes ψ_+ and ψ_- orthogonal. •Make an estimate of the order of magnitude of the integral $\langle\, \psi_{2s}, z\,\psi_{2p_z} \,\rangle$ (and explain how you arrive at this estimate).

d. We suppose now that our hydrogenlike atom is a Cs atom stripped of 54 electrons, i.e., with only one electron in the field of the nucleus with 55 protons. •Find the energy E_1 of the ground state (the $1s$ orbital) in eV. As a measure of the radius of this orbital we could use the quantity a from pkt. **a**, but let us agree that the outer classical turning radius r_y is a better measure (from a chemical point of view). •Find r_y for the $1s$ orbital ixpressed in terms of a_0.



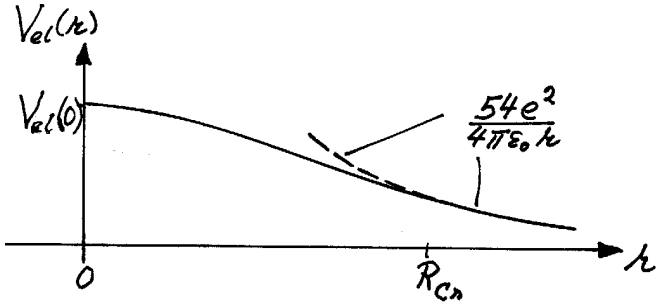
Since the valence orbital of Cs is a $6s$ orbital, it may be interesting to consider the $6s$ orbital of the hydrogenlike atom. The figure shows the radial function $u_{60}(r)$ and the square of it, as functions of r/a_0. •Find the energy E_6 (in eV) and the outer turning radius r_y (expressed in terms of a_0) for u_{60}. •Make an estimate (based on inspection of the figure) of the fraction of the probability outside this turning radius.

e. The results above are of some use when considering the neutral Cs atom, with all 55 electrons around the nucleus. Fyllingsrekkefølgen ??????????????????of orbitals for heavy atoms is

$$1s,\ 2s, 2p,\ 3s, 3p,\ 4s, 3d, 4p,\ 5s, 4d, 5p,\ 6s, 4f, 5d, 6p,\ 7s, 5f, 6d, 7p, \cdots.$$

•Use this to write down the electron configuration ($1s^2, 2s^2$, etc) for the neutral Cs atom.

In addition to the potential $V(r) = -55e^2/(4\pi\epsilon_0 r)$, each electron in Cs "sees" a potential contribution $V_{\rm el}(r)$ due to the charge distribution of the other electrons. Qualitatively this potential contributions looks like this:



Here, $R_{\rm Cs}$ is the "radius" of the Cs atom. Suppose that $V_{\rm el}(r)$ is approximately equal to $V_{\rm el}(0)$ in the region where the $1s$ electrons are moving. •Argue that the $1s$ orbital in this approximation is equal to the wave function ψ_1 from pkt. **a**. •What is (in the same approximation) the energy of the $1s$ orbital? •Why are the distances between the zeros of the $6s$ orbital of Cs larger than the corresponding distances in the figure in pkt. **d**?

Attachment 1: Formulae and expressions **(Some of these formulae may be useful.)**

The Laplace operator and angular momentum operators in spherical coordinates

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

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

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

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

Angular functions

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

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\,\cos\theta = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r} \equiv Y_{p_z}, \qquad Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{\pm i\phi};$$

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

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

Energy eigenfunctions and radial equation, spherically symmetricpotential $V(r)$

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

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

Energy eigenvalues, hydrogenlike system

$$E_n = \frac{E_1}{n^2} \equiv \frac{E_1}{(l+1+n_r)^2}.$$

Some constants

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

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

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