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 FY1006 INNFØRING I KVANTEFYSIKK/ TFY4215 KJEMISK FYSIKK OG KVANTEMEKANIKK onsdag 27. mai 2009

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 page with formulae and expressions is attached (attachment 1)

Sensuren faller i uke 25.

Question 1 (Counts 34 %)



A particle with mass m is moving in a spherical well potential

$$V(r) = \begin{cases} 0 & \text{for } 0 \le r < a, \\ V_0 & \text{for } r > a. \end{cases}$$

This system has energy eigenfunctions on the form

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

where $u_l(r)$ satisfies a radial equation on one-dimensional form:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}}^l(r)\right]u_l(r) = E u_l(r) \qquad \left(u_l(r) \sim r^{l+1} \text{ for small } r\right).$$

Here,

$$V_{\text{eff}}^{l}(r) = V(r) + \frac{\hbar^{2}l(l+1)}{2mr^{2}}$$

is the so-called effective potential.

<u>a.</u> •Explain why possible bound states must have energy $E < V_0$. [Hint: For large r we have approximately that $u_l' \approx (2m/\hbar^2)(V_0 - E)u_l$.]

A solution $u_l(r)$ corresponding to a bound state can not have zeros (nodes) for $r \ge a$ (contrary to bound states). •Explain why, based on the curvature properties for r > a.

<u>b.</u> With a suitable choice of the depth V_0 of the well, one can obtain that a particular radial function corresponding to a bound state for l = 0 looks like this:



(with two nodes for 0 < r < a). •Use the radial equation to find the *form* of this function for r > a, and show that the energy of this state must be approximately equal to V_0 (slightly lower, strictly speaking; cf <u>a</u> above), when you are informed that this function approaches zero for large r, but extremely slowly.

•Find the form of this function $u_b(r)$ also for $0 \le r < a$, and find the depth V_0 of the well, expressed in terms of m and a.

<u>c.</u> •How many *more* eigenfunction solutions with $E < V_0$ does the above radial equation have for l = 0? (Explain.) Make rough sketches of such (possible) additional solutions u(r). •Find an equation which makes it possible to determine wave numbers and energies. (Do not carry through numerical calculations.)

<u>d.</u> •Make a rough sketch of the effective potential $V_{\text{eff}}^{l}(r)$ in the radial equation for l = 1. •Argue that the number of solutions u(r) corresponding to bound states for l = 1 is smaller than for l = 0. •Explain also that when l becomes sufficiently large, then we have no "bound" solutions $u_l(r)$ at all for the system in question.

Question 2 (Counts 24 %)

If a two-atomic molecule is considered as two point masses m_1 and m_2 at a constant distance $|\mathbf{r}| = |\mathbf{r}_1 - \mathbf{r}_2| = R_0$, then the Hamiltonian can be written as

$$\widehat{H} = \frac{\widehat{\mathbf{L}}^2}{2I}.$$

a. •State what I is, expressed in terms of m_1 , m_2 and R_0 . •State what the eigenfunctions of \widehat{H} are, find the energy levels expressed in terms of I and state what the degree of degeneracy is. •What is the physical interpretation of the eigenfunctions?

b. •State what the energies of the ground state and the first and second excited levels are (expressed in terms of I). When a gas of such molecules undergoes de-excitation, a set of spectral lines are emitted. •State what the energies of these spectral lines are (expressed in terms of I). •Find the energy difference between the first excited level and the ground state, in electron volts, when $m_1 = m_2 = 20 m_p$ and $R_0 = 5.5a_0$. (This distance corresponds to a rather loosely bound system.) Given: $m_p \approx 1836 m_e$, $\hbar^2/(2m_e a_0^2) = 13.6$ eV. At room temperature (T = 300 K), two-atomic molecules at equilibrium will have an average rotation energy equal to $k_B T$, where $k_B \approx 8.617 \cdot 10^{-5}$ eV/K is Boltzmann's constant. •To

 $\underline{\mathbf{c.}}$ Suppose that an ensemble of these molecules are prepared in a rotational state described by the angular function

which energy level of the present molecules does this average energy correspond?

$$Y(\theta) = \sqrt{\frac{5}{4\pi}} \, \cos^2 \theta.$$

•Show that this function is normalized. Suppose that the energy is measured for this ensemble. •Find the probabilities of measuring the energies of the ground state, the first excited level, the second excited level etc.

Question 3 (Counts 17 %)

<u>a.</u> A particle with mass m is moving in the one-dimensional oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$. This oscillator is at t = 0 prepared in the normalized state

$$\Psi(x,0) = C_0 \exp[-m\omega(x-x_0)^2/2\hbar].$$

•State the size of the expectation value $\langle x \rangle_0$ at time t = 0. Show that $\langle p_x \rangle_0 = 0$. It can be shown that $\langle p_x^2 \rangle_{\Psi} = \int |\hat{p}_x \Psi|^2 d\tau$ and that

$$\int_{-\infty}^{\infty} (x - x_0)^2 |\Psi(x, 0)|^2 dx = \frac{\hbar}{2m\omega}$$

•Use these relations to find the uncertainties $(\Delta x)_0$ and $(\Delta p_x)_0$ at t = 0, together with the product of these uncertainties.

b. Suppose now that the particle is instead moving in the three-dimensional potential

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

•Find the ground state (expressed in terms of one-dimensional oscillator eigenfuncions; see the formula sheet) and the energy of this state. •Find also the energy, the degree of degeneracy and eigenfunctions for the first excited level.

Question 4 (Counts 20%)

In this question, we will investigate the molecule Ne₂, i.e., the dimer of the noble gas neon. Assume that the molecule lies along the z axis, with the center of mass at the origin. A Hartree-Fock calculation with a large basis set (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, i.e., a total of 19 basis functions pr neon atom) yields a Ne–Ne bond length of 3.25 Å in equilibrium. The mass of a Ne atom is ca 20 m_p . In the LCAO approximation, one constructs the orbital part of the single particle states (i.e., the molecular orbitals – MO) ψ_i as linear combinations of the basis functions ϕ_{μ} :

$$\psi_i = \sum_{\mu=1}^{38} c_{\mu i} \phi_\mu$$

The figure below shows three of the calculated MOs. Light gray denotes a surface of constant negative value of the orbital, black denotes a surface of corresponding constant positive value. (Orientation: z axis horizontally, x axis vertically.)



• What is the parity of ψ_1 , ψ_2 , and ψ_3 (i.e.: even or odd). Give a brief argument for your answer.

Only basis functions of the type p_x and p_z contribute to these three MOs. The coefficients (i.e.: the *c*-s) are all of the same order of magnitude in absolute value, so let us set them equal to +1 or -1. With atom nr 1 to the left and atom nr 2 to the right, the three MOs in the figure above are then (in arbitrary order)

$$\psi_A = p_x^1 + p_x^2$$

$$\psi_B = p_z^1 + p_z^2$$

$$\psi_C = p_x^1 - p_x^2$$

- Which of these are ψ_1 , ψ_2 , and ψ_3 in the figure above?
- Rank the energies of the orbitals ψ_2 and ψ_3 . Give a brief argument for your answer.

The figure on top of the next page shows the calculated Hartree–Fock energy of Ne_2 as a function of the Ne–Ne distance, between 2.8 and 4.5 Å.



Such a form of the interaction potential V(x) between the atoms in a twoatomic molecule is rather well described by the Morse potential

$$V(x) = V_0 \left(1 - e^{-\kappa(x-d)}\right)^2 - V_0.$$

Here, x denotes the distance between the two atoms, whereas V_0 , κ , and d are three (positive) parameters that may be fitted to experimental data or accurate quantum mechanical calculations (as in the figure above).

• Show that the parameter d corresponds to the bond length in equilibrium. What is the depth of this potential, i.e., $V(\infty) - V(d)$?

In the vicinity of equilibrium, the Morse potential may approximately be described as a harmonic oscillator,

$$V(x) \simeq \frac{1}{2} M \omega^2 \left(x - d \right)^2 \quad (+ \text{ const})$$

where M is the oscillator mass (for Ne₂ it equals half the mass of a neon atom).

• Find an expression for ω , and thereby the vibrational frequency $f = \omega/2\pi$ of the twoatomic molecule, within the harmonic approximation. (Hint: Expand the Morse potential around x = d.) Good agreement between the Morse potential and the Hartree–Fock calculations is obtained with $\kappa = 2.25$ Å⁻¹. Use this value and find a numerical value, in the unit eV, for the lowest vibrational energy (the "zero point energy") $E_0 = \hbar \omega/2$ in Ne₂. (Hint: The bond between the neon atoms is weak, so E_0 is not very large. But it is, as expected, considerably larger than the rotational energy that you calculated in question 2**b**.)

Question 5 (Counts 5%)

Many–electron states Ψ must be antisymmetric with respect to interchange of the coordinates of two electrons. Furthermore, Ψ must obey the Pauli principle, i.e., a maximum of one electron in each single particle state ψ . Show that the (Slater) determinant

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix}$$

fulfills these two conditions for a system of two electrons. Here, $\psi_i(j)$ is single particle state nr *i*, and *j* denotes both the position and spin coordinates of electron nr *j*.

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

Relative motion of two-particle system

$$\begin{bmatrix} -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2\mu r^2} + V(\mathbf{r}) \end{bmatrix} \psi(\mathbf{r}) = E\psi(\mathbf{r});$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{(reduced mass);} \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2.$$

Angular functions

$$\begin{cases} \hat{\mathbf{L}}^{2} \\ \hat{L}_{z} \end{cases} Y_{lm} = \begin{cases} \hbar^{2} l(l+1) \\ \hbar m \end{cases} Y_{lm}, \quad l = 0, 1, 2, ...; \qquad \int_{0}^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) Y_{l'm'}^{*} Y_{lm} = \delta_{l'l} \delta_{m'm}; \\ Y_{00} = \sqrt{\frac{1}{4\pi}}, \qquad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \equiv Y_{p_{z}}, \qquad Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}; \\ Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^{2}\theta - 1), \qquad Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi}, \qquad Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^{2}\theta e^{\pm 2i\phi}. \\ \widehat{\mathcal{P}}Y_{lm} = (-1)^{l} Y_{lm}. \end{cases}$$

Selection rules for radiative transitions

$$\Delta l = \pm 1; \qquad \Delta m = 0, \pm 1.$$

Harmonic oscillator

For the potential $V = \frac{1}{2}m\omega^2 x^2$ $(-\infty < x < \infty)$, the energy eigenfunctions satisfy the eigenvalue equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 - (n+\frac{1}{2})\hbar\omega\right]\psi_n(x) = 0, \qquad n = 0, 1, 2, ...,$$

with solutions on the form

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-m\omega x^2/2\hbar} H_n(\xi), \qquad \xi = \frac{x}{\sqrt{\hbar/m\omega}};$$
$$H_0(\xi) = 1, \quad H_1(\xi) = 2\xi, \quad H_2(\xi) = 4\xi^2 - 2, \quad \cdots; \qquad H_n(-\xi) = (-1)^n H_n(\xi).$$

Some constants

 $\hbar = 1$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529 \cdot 10^{-10} \text{ m}; \qquad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.0360};$$
$$\frac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6 \text{ eV}.$$
$$.05 \cdot 10^{-34} \text{ Js}; \qquad e = 1.6 \cdot 10^{-19} \text{ C}; \qquad m_p = 1.67 \cdot 10^{-27} \text{ kg}; \qquad 1 \text{ \AA} = 10^{-10} \text{ m}.$$