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EKSAMEN I
FY1006 INNFØRING I KVANTEFYSIKK/
TFY4215 INNFØRING I KVANTEFYSIKK
Torsdag 31. mai 2012
kl. 9.00 - 13.00

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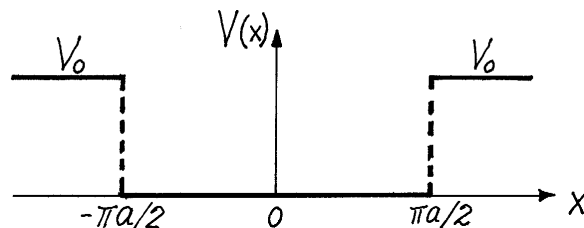Øgrim & Lian: Størrelser og enheter i fysikk og teknikk, eller
Lian og Angell: Fysiske størrelser og enheter;
Aylward & Findlay: SI Chemical Data.

The questions are given in English on pages 1–6. The Norwegian version is also attached.
A sheet with expressions and formulae is attached.

Sensuren faller i uke 25.

Problem 1   (Counts 27 %)

**a.** A particle of mass m is moving in a simple one-dimensional spherical well potential

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

The width (πa) of the well is chosen in such a way that this system has an energy eigenfunction (which we may call ψ_2) with the energy $E_2 = V_0$. ♠Show, using the time-independent Schrödinger equation, that ψ_2 must have the form $\psi_2 = B$ (a constant) for $x > \pi a/2$. ♠Then find the form of ψ_2 inside the well, for $-\pi a/2 < x < \pi a/2$. ♠Make a sketch of the function ψ_2, and explain in words how it behaves for $x < -\pi a/2$.

b. The function ψ_2 actually is the first excited state of this system. ♠Find out what are the forms of the ground state ψ_1 inside and outside the well, and make a sketch of ψ_1. ♠Find an equation which determines the energy of the ground state, and explain how this equation can be solved (without actually carrying through the calculation).

c. We now modify the potential, by adding a barrier of height $2V_0 = \hbar^2/(ma^2)$ in the middle of the well, in the region $-b < x < b$, where $0 < b < \pi a/2$; see the figure:
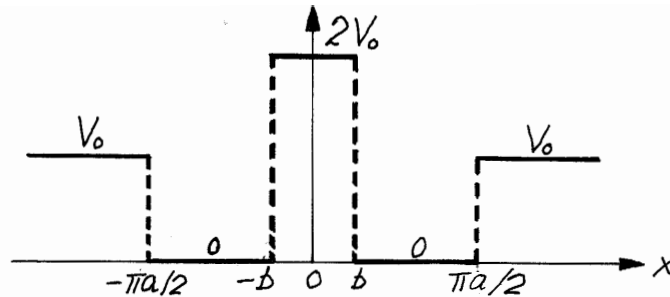
When b is increased from zero, the ground-state energy E_1 will increase. We shall now see how one can find the b-value (b_0) which makes $E_1 = V_0$. You are informed that the ground state ψ_1 is symmetric for all $0 \le b \le b_0$. ♠Assume that $E_1 = V_0$, and start by finding what the form of ψ_1 is for $|x| > \pi a/2$. ♠Then show that ψ_1 for $b_0 < x < \pi a/2$ is proportional to $\sin k_1 x$ (where k_1 should be determined). Go on to find the form for $-b_0 < x < b_0$. [You might find it helpful to make a sketch.] ♠Find at last an equation which determines b_0. (You are not asked to solve this equation.)

Problem 2   (Counts 16 %)

In this Problem, we consider a two-dimensional system, where a particle of mass m is moving in the xy-plane, in a harmonic oscillator potential $V(x,y) = \frac{1}{2}m\omega^2(x^2 + y^2)$. At $t = 0$, this oscillator is prepared in the product state $\Psi(x,y,0) = \psi_x(x)\psi_y(y)$, where both ψ_x and ψ_y are normalized:

$$\psi_x(x) = C_0 \exp[-m\omega(x - b)^2/2\hbar] \qquad \left(C_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\right),$$

$$\psi_y(y) = C_0 \exp[-m\omega y^2/2\hbar + iy\,m\omega b/\hbar], \qquad (b > 0).$$

a. ♠Explain which symmetry properties the probability density $|\Psi(x,y,0)|^2$ at $t = 0$ has, and use these properties to find the expectation values $\langle x \rangle_0$ and $\langle y \rangle_0$ at $t = 0$ (without explicit calculations). ♠Show that $\langle p_x \rangle_0 = 0$ and $\langle p_y \rangle_0 = m\omega b$. [Hint: Note that (e.g.)

$$\langle f(x, p_x) \rangle_0 = \int_{-\infty}^{\infty} \psi_x^*(x)\, f(x, \hat{p}_x)\, \psi_x(x)dx,$$

multiplied by the normalization integral for $\psi_y(y)$, which is equal to 1.]

b. ♠Use Ehrenfest's theorem to show that the expectation values of x and p_x for $t > 0$ for this oscillator can be written on the form

$$\langle x_t \rangle = A_x \sin \omega t + B_x \cos \omega t; \qquad \langle p_x \rangle_t = m\omega(A_x \cos \omega t - B_x \sin \omega t).$$

♠Use the above results to determine A_x and B_x, find corresponding results for the y-direction, and show that the expectation value of the position follows a circular orbit.

Problem 3   (Counts 32 %)

In this Problem we consider first a hydrogenlike atom consisting of a cesium nucleus $(Z = 55)$ and an electron. A measurement is carried out of the energy E, the square $\mathbf{L}^2$ of the angular momentum and a certain component $\hat{\mathbf{n}}{\cdot}\mathbf{L}$ of this, on a large number of such hyrogenlike atoms. A *selection* of these atoms will then be left in an ensemble described by the wave function

$$\psi = R(r)Y(\theta, \phi),$$

where

$$R = C\frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right)\exp(-Zr/3a_0)$$

and

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

Here, C ia a normalization constant and $\hat{\mathbf{n}}$ is a unit vector.

a.   The radial function given above implies that the reduced mass has been set equal to the electron mass m_e. ♠Why is this a very good approximation for the present system? ♠What do we mean by stating that E, $\mathbf{L}^2$ and $\hat{\mathbf{n}}{\cdot}\mathbf{L}$ are *compatible observables* for the present system, and what are the conditions satisfied by the corresponding operators? ♠What is the result for $\mathbf{L}^2$ measured in the preparation of this ensemble, and what is the corresponding angular-momentum quantum number l? (Explain your answer.) ♠Find the radial quantum number n_r and the energy E which was measured in the preparation of this ensemble, using the formula sheet.

b.   In analogy with the fact that $\widehat{L}_z = (\hbar/i)\partial/\partial\phi$ "asks for" the variation in the azimuthal direction, that is, the variation following a rotation about the z-axis, we can set

$$\hat{\mathbf{n}}{\cdot}\widehat{\mathbf{L}} = \frac{\hbar}{i}\frac{\partial}{\partial\phi'},$$

where the angle ϕ' describes rotation about the $\hat{\mathbf{n}}$-axis. ♠Based on this, argue that the result measured for $\hat{\mathbf{n}}{\cdot}\mathbf{L}$ was equal to zero. Suppose that L_z is measured for the ensemble which was prepared in the state $\psi = RY$. ♠Find the possible measured results and the corresponding probabilities. ♠Find also the expectation value $\langle\, L_z\,\rangle$ for the state $\psi = RY$.

c.   At last, let us make a small comparison between the hydrogenlike atom $(Z = 55)$ and the *neutral* cesium atom. The most loosely bound electron of the cesium atom is in the $6s$ orbital,

$$\psi_{600}^{\mathrm{Cs}} = R_{60}^{\mathrm{Cs}}Y_{00} \equiv \frac{u_{60}^{\mathrm{Cs}}}{r}\,Y_{00},$$

where the radial function has $n_r = n - l - 1 = 5$ zeros. For s-waves, the functions $u_{n0} = rR_{n0}$ satisfy the "one-dimensional" equation

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} + V(r)\right]u_{n0} = E\,u_{n0}, \qquad (l = 0),$$

where $V(r)$ is the potential due to the nucleus in the hydrogenlike case, and due to the nucleus plus the 54 other electrons in the Cs case. ♠Start by explaining what we mean by the *relative curvature* of a radial function $u(r) = rR(r)$, and find the relative curvature expressed in terms of the kinetic energy $E - V(r)$ for the *s*-waves u_{n0}. ♠How does u curve in classically and forbidden regions?
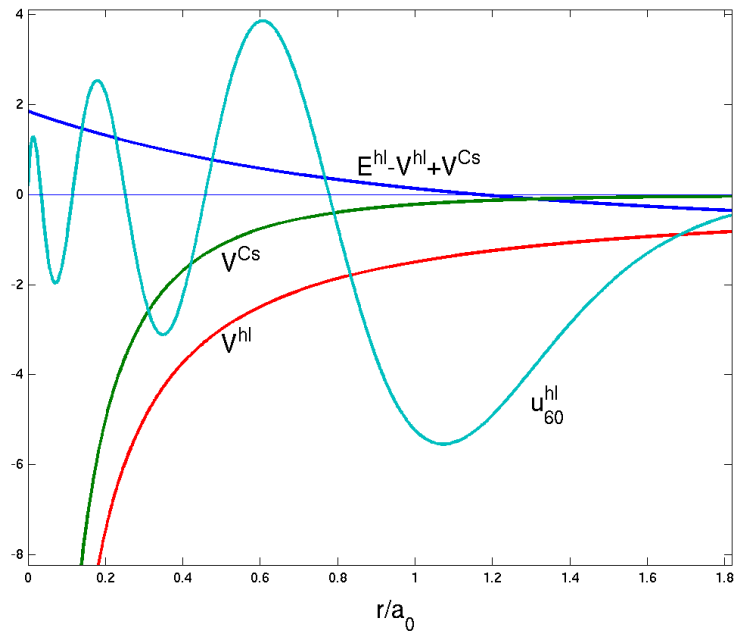
In the figure,

$$V^{\mathrm{hl}} = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Z\hbar^2}{m_e a_0 r} \qquad (Z = 55)$$

is the unscreened Coulomb potential for the hydrogenlike atom (in units of keV). The curve u_{60}^{hl} is the corresponding $6s$ state. ♠*Estimate* the outer turning radius $r_{\mathrm{outer}}^{\mathrm{hl}}$ for this state using the diagram, and *calculate* the same quantity, as a check. ♠Why must the zeros of this radial function lie between zero and $r_{\mathrm{outer}}^{\mathrm{hl}}$? ♠Why are the distances between the zeros smallest for small r?

<u>**d.**</u> The curve V^{Cs} shows a simplified model of the potential which the $6s$ electron in Cs experiences (in keV). Note that for large r, $V^{\mathrm{Cs}}[\approx -e^2/4\pi\epsilon_0 r]$ is much weaker than $V^{\mathrm{hl}}[= -Ze^2/4\pi\epsilon_0 r]$. ♠Explain why.

The difference between the *binding energies* of the two $6s$ states is even bigger: For the hydrogenlike atom, $-E^{\mathrm{hl}}$ is more than 1 keV, while $-E^{\mathrm{Cs}}$ in reality is of the order of $5\,\mathrm{eV}$. In order to understand how this can be, it is important to note that the difference between the kinetic energies in the two cases satisfies the following inequality (using that $-E^{\mathrm{Cs}} \sim 5\,\mathrm{eV} > 0$):

$$E^{\mathrm{hl}} - V^{\mathrm{hl}} - (E^{\mathrm{Cs}} - V^{\mathrm{Cs}}) \; > \; E^{\mathrm{hl}} - V^{\mathrm{hl}} + V^{\mathrm{Cs}}.$$

The right-hand side of this inequality is shown in the figure above (in the simplified model we are using, and in units of keV). ♠Explain on the basis of this why the zeros of u_{60}^{Cs} must lie futher out than the corresponding zeros of u_{60}^{hl}. ♠What must we then expect (qualitatively) when comparing the outer turning radius $r_{\mathrm{outer}}^{\mathrm{Cs}}$ with $r_{\mathrm{outer}}^{\mathrm{hl}}$, and comparing E^{Cs} with E^{hl}?

Problem 4 (Counts 25%)

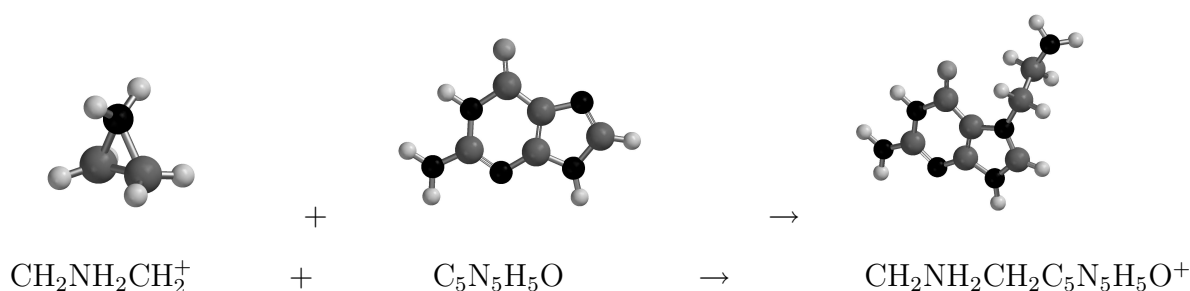*Introduction (not really necessary for solving the problems):*
The poisonous *mustard gas* $ClCH_2CH_2SCH_2CH_2Cl$ is, by substitution of the S atom with NR (where R = H, CH_3, or a larger alkyl group), changed into *amines*, that happen to be quite effective within chemotherapy and cancer treatment. This question is related to the mechanism for how such amines react with *guanine*, which is one of the four types of bases in DNA.

The reaction starts by the formation of a so called *aziridinium* cation (see figure below, left, where R = CH_3) when a chloride ion Cl^- leaves the amine molecule. A three-atomic ring (N-C-C) is created, and the reaction with guanine in DNA proceeds through the formation of a chemical bond between one of the C atoms in the three-membered ring and one of the N atoms of guanine. We have been asked to examine this reaction more closely, and since we do not have a laboratory at our disposal, but on the other hand a computer, we choose to perform the necessary quantum mechanical calculations with the Hartree–Fock method. First, we replace the two groups CH_3 and CH_2CH_2Cl with two H atoms (see figure below, right), in order to reduce the computational time.

$$CH_2(NCH_3CH_2CH_2Cl)CH_2^+ \qquad CH_2NH_2CH_2^+$$
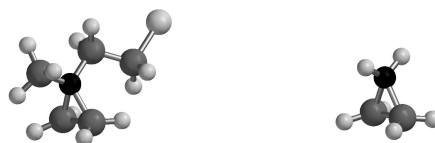
Hence, the reaction becomes:

$$CH_2NH_2CH_2^+ \qquad + \qquad C_5N_5H_5O \qquad \rightarrow \qquad CH_2NH_2CH_2C_5N_5H_5O^+$$

(Size, color: C: large, gray; N: medium, black; O: medium, light gray; H: small, white; Cl: large, white)

Here, the introduction to the question ends!

In the basis set 3–21G(*), one includes the atomic orbitals, or *basis functions*, 1s and 2s for each H atom, and 1s, 2s, 2p, 3s, and 3p for each C, N, and O atom. ♠How many basis functions are then included in the calculation for, respectively,

- $CH_2NH_2CH_2^+$, $\qquad$ • $C_5N_5H_5O$, $\qquad$ • $CH_2NH_2CH_2C_5N_5H_5O^+$?

♠How many electrons are there in, respectively,

- $CH_2NH_2CH_2^+$,   • $C_5N_5H_5O$,   • $CH_2NH_2CH_2C_5N_5H_5O^+$?

For each of these three molecules, the total electron spin S is zero in the ground state. ♠Explain why $S = 0$ is possible here.   ♠Could one for these molecules imagine a ground state with total electron spin $S = 1/2$? What about $S = 1$? Explain your answers briefly. ♠In the ground state, with $S = 0$, how many molecular orbitals are occupied by electrons in, respectively,

- $CH_2NH_2CH_2^+$,   • $C_5N_5H_5O$,   • $CH_2NH_2CH_2C_5N_5H_5O^+$?

(Remember the Pauli principle!)

♠How many vibrational degrees of freedom are there in, respectively,

- $CH_2NH_2CH_2^+$,   • $C_5N_5H_5O$,   • $CH_2NH_2CH_2C_5N_5H_5O^+$?

In a Hartree–Fock calculation, we may roughly assume that the computational time depends on the number of basis functions raised to the power four.   ♠If a computation on $CH_2NH_2CH_2^+$ lasts for one second, how long time will a computation then roughly last for $CH_2NH_2CH_2C_5N_5H_5O^+$?

Our computations on the above described chemical reaction, where we change the distance between the N atom in guanine and the C atom in $CH_2NH_2CH_2^+$ stepwise from 2.8 Å to 1.5 Å, result in the following energy curve:
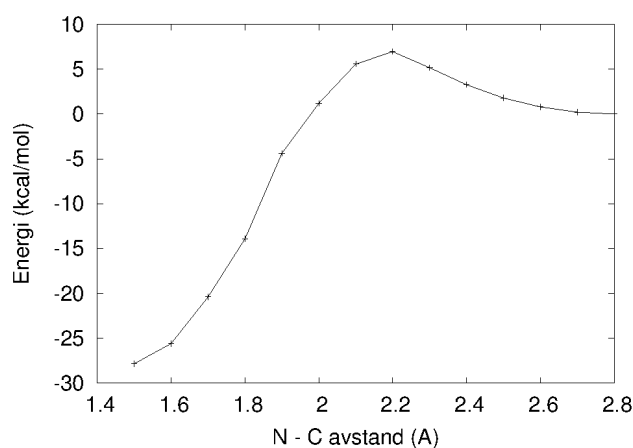
♠From the figure, read off the activation energy E_a of this reaction, and next, calculate the corresponding Boltzmann factor $\exp(-E_a/k_BT)$ at room temperature. ♠Based on this, may we conclude that the modeled reaction is not going to happen at room temperature? Assume ideal gas behavior, $pV = Nk_BT$, calculate the volume pr molecule (assuming a normal pressure p), estimate thus a mean free path between two collisions for a given molecule, and hence an average time τ between subsequent collisions. Remember that the temperature T is directly related to the average kinetic energy of the molecules.

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

One-dimensional harmonic oscillator, $V(x) = \frac{1}{2}kx^2$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}kx^2\right)\psi_n(x) = \hbar\omega(n+\tfrac{1}{2})\psi_n(x); \qquad \omega = \sqrt{\frac{k}{m}}; \qquad (\psi_n, \psi_k) = \delta_{nk};$$

$$\psi_0(x) = C_0\, e^{-m\omega x^2/2\hbar}, \qquad C_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4};$$

$$\psi_1(x) = C_0\sqrt{\frac{2m\omega}{\hbar}}\, x\, e^{-m\omega x^2/2\hbar}, \qquad \psi_2(x) = \frac{C_0}{2}\left(\frac{2m\omega}{\hbar}x^2 - 1\right)e^{-m\omega x^2/2\hbar}, \cdots;$$

$$\psi_n(-x) = (-1)^n\psi_n(x).$$

The Laplace operator and angular-momentum operators in polar coordinates

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

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

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

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

Hydrogenlike system

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Z\hbar^2}{m_e a_0 r}; \qquad E_n = -\tfrac{1}{2}(\alpha Z)^2\frac{mc^2}{n^2} = -\frac{\hbar^2}{2m_e a_0^2}\frac{m}{m_e}\frac{Z^2}{(l+1+n_r)^2}.$$

$[m = m_1 m_2/(m_1 + m_2)$ is the reduced mass; n_r is the number of zeros in the radial function, for $0 < r < \infty$.]

Angular functions

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

$$Y_{00} = \sqrt{\frac{1}{4\pi}}, \qquad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \equiv Y_{p_z}, \qquad Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi};$$

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

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \qquad Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}, \qquad Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}.$$

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

Ehrenfest's theorem

$$\frac{d}{dt}\langle\,\mathbf{r}\,\rangle_t = \frac{\langle\,\mathbf{p}\,\rangle_t}{m} \qquad \text{and} \qquad \frac{d}{dt}\langle\,\mathbf{p}\,\rangle_t = \langle\,-\boldsymbol{\nabla}V\,\rangle_t\,.$$

Some constants

$$\hbar = 1.054\,571\,68(18)\cdot 10^{-34}\,\text{Js} = 6.582\,119\,15(56)\cdot 10^{-16}\text{eVs};$$

$$1\,\text{eV} = 1.602\,176\,53(14)\cdot 10^{-19}\,\text{J} \approx 0.03676\,\text{hartree} \approx 23.07\,\text{kcal/mol};$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529177\cdot 10^{-10}\,\text{m} \qquad \text{(Bohr radius)};$$

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

$$\tfrac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6057\,\text{eV} \qquad \text{(Rydberg energy)};$$

$$k_B = 1.381\cdot 10^{-23}\,\text{J/K} = 8.625\cdot 10^{-5}\,\text{eV/K} \qquad \text{(Boltzmann's constant)};$$

$$u = 1.661\cdot 10^{-27}\,\text{kg} \qquad \text{(atomic mass unit)};$$

$$1\,\text{atm} = 1.013\cdot 10^5\,\text{N/m}^2;$$

$$1\,\text{Å} = 10^{-10}\,\text{m}.$$

Some formulae

$$\tan y = \frac{1}{\cot y} = \tan(y + n\pi), \quad n = 0, \pm1, \cdots;$$

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

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