

NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET  
 Institutt for fysikk

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**EKSAMEN I**  
**FY1006 INNFORING I KVANTEFYSIKK/**  
**TFY4215 INNFORING I KVANTEFYSIKK**

Torsdag 31. mai 2012

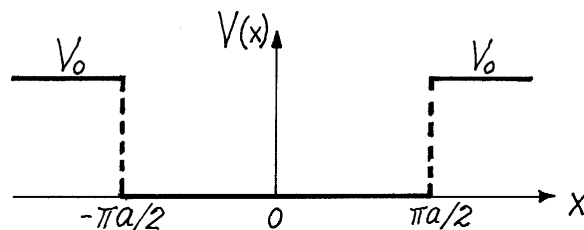
kl. 9.00 - 13.00

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.

Et ark med uttrykk og formler er heftet ved.

Sensuren faller i uke 25.

**Oppgave 1** (Teller 27 %)



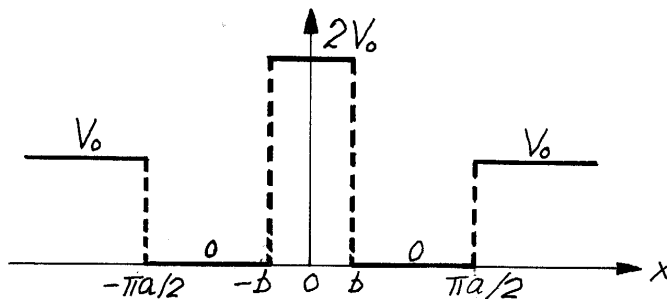
**a.** En partikkel med masse  $m$  befinner seg i et enkelt endimensjonalt brønnpotensial

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

Brønnvidden ( $\pi a$ ) er valgt slik at dette systemet har en energieigenfunksjon (som vi kan kalle  $\psi_2$ ) med energien  $E_2 = V_0$ . ♠ Vis ved hjelp av den tidsuavhengige Schrödingerligningen at  $\psi_2$  må ha formen  $\psi_2 = B$  (en konstant) for  $x > \pi a/2$ . ♠ Finn deretter formen til  $\psi_2$  i brønnområdet,  $-\pi a/2 < x < \pi a/2$ . ♠ Tegn en skisse av funksjonen  $\psi_2$ , og forklar med ord hvordan den oppfører seg for  $x < -\pi a/2$ .

**b.** Funksjonen  $\psi_2$  er i realiteten 1. eksiterte tilstand for dette systemet. ♠ Finn ut hvilken form grunntilstanden  $\psi_1$  må ha i og utenfor brønnen, og skissér  $\psi_1$ . ♠ Finn en ligning som bestemmer grunntilstandsenergien, og forklar hvordan denne kan løses (uten å gjennomføre beregningen).

**c.** Vi modifierer nå potensialet, ved å plassere en barriere med høyde  $2V_0 = \hbar^2/(ma^2)$  midt i brønnen, i området  $-b < x < b$ , der  $0 < b < \pi a/2$ ; se figuren:



Når  $b$  økes fra null, vil grunntilstandsenergien  $E_1$  øke. Vi skal nå se hvordan en kan finne den  $b$ -verdien ( $b_0$ ) som gir  $E_1 = V_0$ . Det opplyses at grunntilstanden  $\psi_1$  er symmetrisk for alle  $0 \leq b \leq b_0$ . ♠ Anta at  $E_1 = V_0$ , og finn først ut hvilken form  $\psi_1$  har for  $|x| > \pi a/2$ . ♠ Vis deretter at  $\psi_1$  for  $b_0 < x < \pi a/2$  er proporsjonal med  $\sin k_1 x$  (der  $k_1$  skal bestemmes). Finn så formen for  $-b_0 < x < b_0$ . [Det kan hjelpe å lage en skisse.] ♠ Finn til slutt en ligning som bestemmer  $b_0$ . (Denne kreves ikke løst.)

## Oppgave 2 (Teller 16 %)

I denne oppgaven betrakter vi en todimensjonal problemstilling, der en partikkel med masse  $m$  beveger seg i  $xy$ -planet, i et harmonisk oscillatorpotensial  $V(x, y) = \frac{1}{2}m\omega^2(x^2 + y^2)$ . Ved  $t = 0$  prepareres denne oscillatoren i produkt-tilstanden  $\Psi(x, y, 0) = \psi_x(x)\psi_y(y)$ , der både  $\psi_x$  og  $\psi_y$  er normerte:

$$\begin{aligned} \psi_x(x) &= C_0 \exp[-m\omega(x-b)^2/2\hbar] & \left( C_0 = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \right), \\ \psi_y(y) &= C_0 \exp[-m\omega y^2/2\hbar + iy m\omega b/\hbar], & (b > 0). \end{aligned}$$

**a.** ♠ Forklar hvilke symmetriegenskaper sannsynlighetstettheten  $|\Psi(x, y, 0)|^2$  ved  $t = 0$  har, og bruk dette til å finne forventningsverdiene  $\langle x \rangle_0$  og  $\langle y \rangle_0$  ved  $t = 0$  (uten å regne eksplisitt). ♠ Vis at  $\langle p_x \rangle_0 = 0$  og  $\langle p_y \rangle_0 = m\omega b$ . [Hint: Merk at (f.eks)

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

multiplisert med normeringsintegralet for  $\psi_y(y)$ , som jo er lik 1.]

**b.** ♠ Bruk Ehrenfests teorem til å vise at forventningsverdiene av  $x$  og  $p_x$  for  $t > 0$  for denne oscillatoren kan skrives på formen

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

♠ Bruk resultatene ovenfor til å bestemme  $A_x$  og  $B_x$ , finn tilsvarende resultater for  $y$ -retningen, og vis at forventningsverdien av posisjonen følger en sirkelbane.

### Oppgave 3 (Teller 32 %)

I denne oppgaven ser vi først på et hydrogenlignende atom som består av en cesium-kjerne ( $Z = 55$ ) og et elektron. Det gjøres en måling av energien  $E$ , kvadratet  $\mathbf{L}^2$  av dreieimpulsen og en viss komponent  $\hat{\mathbf{n}} \cdot \mathbf{L}$  av denne, på et stort antall av slike atomer. Et *utvalg av dem* havner da i et ensemble beskrevet av bølgefunksjonen

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

der

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

og

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

Her er  $C$  en normeringskonstant og  $\hat{\mathbf{n}}$  en enhetsvektor.

**a.** Radialfunksjonen ovenfor svarer til at den reduserte massen er satt lik elektronmassen  $m_e$ . ♠ Hvorfor er dette en svært god tilnærming i denne problemstillingen? ♠ Hva mener vi med å si at  $E$ ,  $\mathbf{L}^2$  og  $\hat{\mathbf{n}} \cdot \mathbf{L}$  er *kompatible observable* for dette systemet, og hvilke betingelser svarer dette til for de tilsvarende operatorene? ♠ Hva er måleresultatet for  $\mathbf{L}^2$  ved prepareringen av dette ensemblet, og hva er det tilhørende dreieimpulsquantetallet  $l$ ? (Begrunn svaret.) ♠ Finn radiale kvantetallet  $n_r$ , og finn energien  $E$  som ble målt ved prepareringen av dette ensemblet, ved hjelp av formelarket.

**b.** Analogt med at  $\hat{L}_z = (\hbar/i)\partial/\partial\phi$  "spør etter" variasjonen i asimut-retningen, dvs variasjon ved rotasjon omkring  $z$ -aksen, kan vi sette

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

der vinkelen  $\phi'$  beskriver rotasjon rundt  $\hat{\mathbf{n}}$ -aksen. ♠ Argumentér ut fra dette for at måleresultatet for  $\hat{\mathbf{n}} \cdot \mathbf{L}$  var lik null. Anta at  $L_z$  måles for ensemblet som er preparert i tilstanden  $\psi = RY$ . ♠ Finn de mulige måleresultatene og de tilhørende sannsynlighetene. ♠ Finn også forventningsverdien  $\langle L_z \rangle$  for tilstanden  $\psi = RY$ .

**c.** La oss til slutt gjøre en liten sammenligning av det hydrogenlignende atomet ( $Z = 55$ ) og det *nøytrale* cesium-atomet. Det løsest bundne elektronet i cesium befinner seg i  $6s$ -orbitalen,

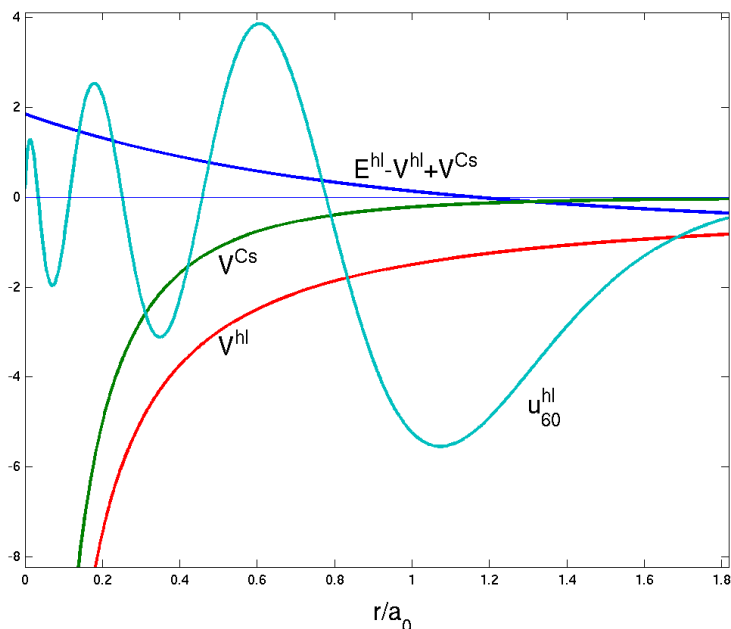
$$\psi_{600}^{\text{Cs}} = R_{60}^{\text{Cs}} Y_{00} \equiv \frac{u_{60}^{\text{Cs}}}{r} Y_{00},$$

hvor radialfunksjonen har  $n_r = n - l - 1 = 5$  nullpunkter. For  $s$ -bølger oppfyller funksjonene  $u_{n0} = rR_{n0}$  den "endimensjonale" ligningen

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

der  $V(r)$  er potensialet fra kjernen i det hydrogenlignende tilfellet, og fra kjernen og de 54 øvrige elektronene i Cs-tilfellet.

♠ Forklar først hva vi mener med den *relative krumningen* av en radialfunksjon  $u(r) = rR(r)$ , og finn den relative krumningen uttrykt ved den kinetiske energien  $E - V(r)$  for  $s$ -bølgene  $u_{n0}$ . ♠ Hvordan krummer  $u$  i klassisk tillatte og klassisk forbudte områder?



I figuren er

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

det uskjermede Coulomb-potensialet for det hydrogenlignende atomet (i enheter av keV). Kurven  $u_{60}^{\text{hl}}$  er den tilsvarende  $6s$ -tilstanden. ♠ Anslå den ytre venderadien  $r_{\text{ytre}}^{\text{hl}}$  for denne tilstanden ut fra diagrammet, og *beregn* den samme størrelsen, som en kontroll. ♠ Hvorfor må nullpunktene i denne radialfunksjonen ligge innenfor  $r_{\text{ytre}}^{\text{hl}}$ ? ♠ Hvorfor ligger disse nullpunktene tettest for små  $r$ ?

**d.** Kurven  $V^{\text{Cs}}$  viser en forenklet modell av potensialet som  $6s$ -elektronet i Cs opplever (i keV). Merk at for store  $r$  er  $V^{\text{Cs}}[\approx -e^2/4\pi\epsilon_0 r]$  mye svakere enn  $V^{\text{hl}}[= -Ze^2/4\pi\epsilon_0 r]$ . ♠ Forklar hvorfor.

Enda større forskjell er det mellom *bindingsenergiene* til de to  $6s$ -tilstandene: For det hydrogenlignende atomet er  $-E^{\text{hl}}$  mer enn 1 keV, mens  $-E^{\text{Cs}}$  i virkeligheten er av størrelsesorden 5 eV. Når vi skal prøve å skjønne hvordan dette henger sammen, er det et viktig poeng at differansen mellom de kinetiske energiene i de to tilfellene oppfyller følgende ulikhet (idet  $-E^{\text{Cs}} \sim 5 \text{ eV} > 0$ ):

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

Høyresiden i denne ulikheten er vist i figuren ovenfor (i den nevnte forenklete modellen, og i enheter av keV). ♠ Forklar på bakgrunn av dette hvorfor nullpunktene i  $u_{60}^{\text{Cs}}$  må ligge lenger ut enn de tilsvarende nullpunktene i  $u_{60}^{\text{hl}}$ . ♠ Hva må vi da (kvalitativt) forvente når det gjelder venderadien  $r_{\text{ytre}}^{\text{Cs}}$  i forhold til  $r_{\text{ytre}}^{\text{hl}}$ , og når det gjelder  $E^{\text{Cs}}$  i forhold til  $E^{\text{hl}}$ ?

## Oppgave 4 (Teller 25%)

*Innledning (strengt tatt ikke nødvendig for å løse oppgaven):*

Den giftige *sennepsgassen*  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$  blir ved å erstatte S-atomet med NR (der  $\text{R} = \text{H}$ ,  $\text{CH}_3$  eller en større alkylgruppe) omdannet til *aminer* som har vist seg meget effektive innen kjemoterapi og bekjempelse av kreft. Denne oppgaven er knyttet til mekanismen for hvordan slike aminer reagerer med *guanin*, som er en av fire typer baser som inngår i DNA.

Det viser seg at reaksjonen starter med dannelsen av et såkalt *aziridinium* kation (se figuren nedenfor, til venstre, der  $\text{R} = \text{CH}_3$ ) ved at et kloridion  $\text{Cl}^-$  spaltes av aminet. En tre-atomig ring (N-C-C) dannes, og reaksjonen med guanin i DNA forløper ved at en kjemisk binding dannes mellom et av C-atomene i den tre-atomige ringen og et av N-atomene i guanin. Vi har fått i oppdrag å studere denne reaksjonen nærmere, og siden vi ikke har et laboratorium men derimot en datamaskin til rådighet, velger vi å gjøre de nødvendige kvantemekaniske beregninger med Hartree–Fock–metoden. Vi erstatter først de to gruppene  $\text{CH}_3$  og  $\text{CH}_2\text{CH}_2\text{Cl}$  med to H-atomer (se figuren nedenfor, til høyre) for å redusere regnetiden.



Reaksjonen blir dermed:



+



→



(Størrelse og farge: C: stor, grå; N: medium, svart; O: medium, lys grå; H: liten, hvit; Cl: stor, hvit)

*Her slutter innledningen til oppgaven!*

I basissettet 3–21G(\*) inkluderer man de atomære orbitalene, eller *basisfunksjonene*, 1s og 2s for hvert H-atom, og 1s, 2s, 2p, 3s og 3p for hvert C-, N- og O-atom. ♠Hvor mange basisfunksjoner inkluderes da i beregningen for henholdsvis

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,      •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,      •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

♠Hvor mange elektroner er det i alt i henholdsvis

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

For hvert av disse tre molekylene er det totale spinnet  $S$  til elektronene i grunntilstanden lik null. ♠Forklar hvorfor  $S = 0$  her er mulig. ♠Kunne man her tenke seg en grunntilstand med totalt elektronspinn  $S = 1/2$ ? Hva med  $S = 1$ ? Begrunn svarene dine. ♠I grunntilstanden, med  $S = 0$ , hvor mange molekylorbitaler er okkupert av elektroner, i henholdsvis

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

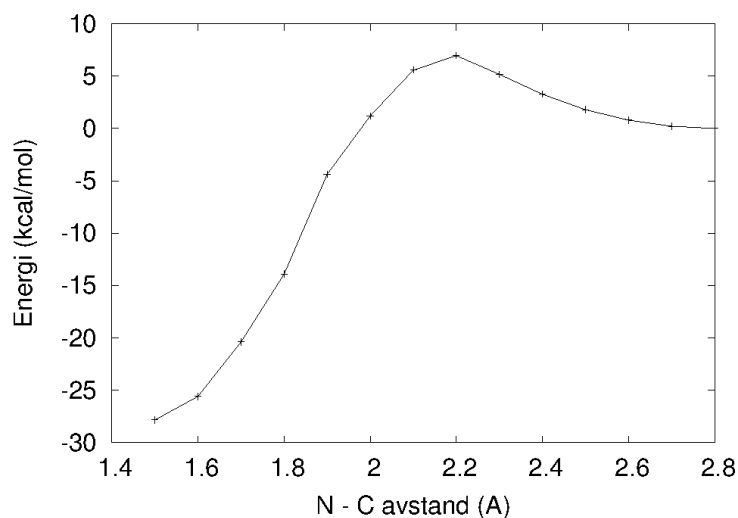
(Husk Pauliprinsippet!)

♠Hvor mange vibrasjonsfrihetsgrader er det i henholdsvis

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

I en Hartree-Fock-beregning kan vi grovt sett anta at beregningstiden avhenger av antall basisfunksjoner opphøyd i fjerde potens. ♠Dersom en beregning på  $\text{CH}_2\text{NH}_2\text{CH}_2^+$  tar ett sekund, hvor lang tid vil da en beregning omtrent ta for  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$ ?

Vår beregning av den beskrevne kjemiske reaksjonen, der vi endrer avstanden mellom N-atomet i guanin og C-atomet i  $\text{CH}_2\text{NH}_2\text{CH}_2^+$  skrittvis fra 2.8 Å til 1.5 Å, resulterer i følgende energikurve:



♠Les av reaksjonens aktiveringsenergi  $E_a$  fra figuren (på øyemål) og regn deretter ut den tilhørende Boltzmannfaktoren  $\exp(-E_a/k_B T)$  ved romtemperatur. ♠Kan vi ut fra dette konkludere med at den modellerte reaksjonen ikke vil skje ved romtemperatur? Anta ideell gass,  $pV = Nk_B T$ , regn ut volumet pr molekyl (ved normalt trykk  $p$ ), anslå fra dette en midlere fri veilengde mellom to kollisjoner for et gitt molekyl, og dermed en midlere tid  $\tau$  mellom påfølgende kollisjoner. Husk at temperaturen  $T$  er direkte knyttet til molekylene's midlere kinetiske energi.

## Vedlegg: Formler og uttrykk (Noe av dette kan du få bruk for.)

Endimensjonal harmonisk oscillator,  $V(x) = \frac{1}{2}kx^2$

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

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

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

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

Laplace-operatoren og dreieimpulsoperatører i kulekoordinater

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

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

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

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

Hydrogenlignende system

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

[ $m = m_1 m_2 / (m_1 + m_2)$  er den reduserte massen;  $n_r$  er antall nullpunkter i radialfunksjonen, for  $0 < r < \infty$ .]

Vinkelfunksjoner

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

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

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

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

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

## Ehrenfests teorem

$$\frac{d}{dt} \langle \mathbf{r} \rangle_t = \frac{\langle \mathbf{p} \rangle_t}{m} \quad \text{og} \quad \frac{d}{dt} \langle \mathbf{p} \rangle_t = \langle -\nabla V \rangle_t.$$

## Noen konstanter

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

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

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

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

$$\frac{1}{2}\alpha^2 m_e c^2 = \frac{\hbar^2}{2m_e a_0^2} \approx 13.6057 \text{ eV} \quad (\text{Rydberg-energien});$$

$$k_B = 1.381 \cdot 10^{-23} \text{ J/K} = 8.625 \cdot 10^{-5} \text{ eV/K} \quad (\text{Boltzmanns konstant});$$

$$u = 1.661 \cdot 10^{-27} \text{ kg} \quad (\text{atomær masse-enhet});$$

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

$$1 \text{ \AA} = 10^{-10} \text{ m}.$$

## Noen formler

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

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

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



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Rottmann: Matematisk formelsamling;

Øgrim & Lian: Størrelser og enheter i fysikk og teknikk, eller

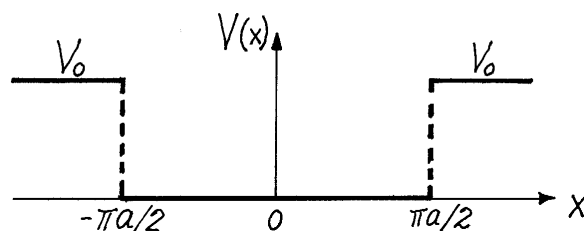
Lian og Angell: Fysiske størrelser og enheter;

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 %)



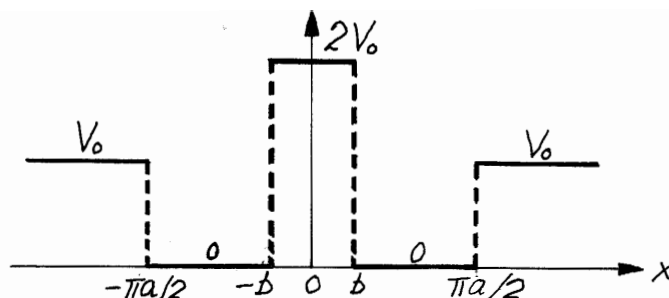
**a.** A particle of mass  $m$  is moving in a simple one-dimensional spherical well potential

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

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

**b.** The function  $\psi_2$  actually is the first excited state of this system. ♠ Find out what are the forms of the ground state  $\psi_1$  inside and outside the well, and make a sketch of  $\psi_1$ . ♠ 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  $\psi_1$  is symmetric for all  $0 \leq b \leq b_0$ . ♠ Assume that  $E_1 = V_0$ , and start by finding what the form of  $\psi_1$  is for  $|x| > \pi a/2$ . ♠ Then show that  $\psi_1$  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  $\psi_x$  and  $\psi_y$  are normalized:

$$\begin{aligned} \psi_x(x) &= C_0 \exp[-m\omega(x-b)^2/2\hbar] & \left( C_0 = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \right), \\ \psi_y(y) &= C_0 \exp[-m\omega y^2/2\hbar + iy m\omega b/\hbar], & (b > 0). \end{aligned}$$

**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

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

♠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 hydrogenlike 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,  $C$  is 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  $\hat{L}_z = (\hbar/i)\partial/\partial\phi$  “asks for” the variation in the azimuthal direction, that is, the variation following a rotation about the  $z$ -axis, we can set

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

where the angle  $\phi'$  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  $\psi = RY$ .

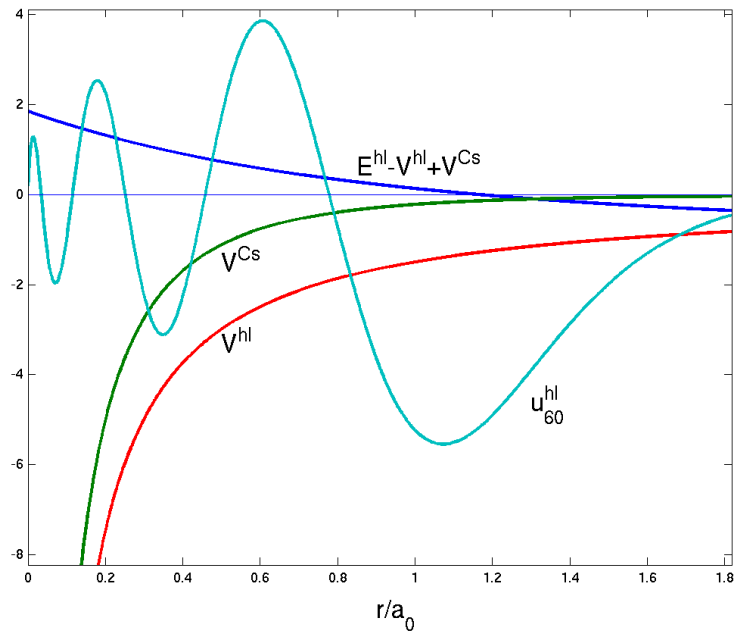
**c.** At last, let us make a small comparison between the hydrogenlike atom ( $Z = 55$ ) and the *neutral* cesium atom. The most loosely bound electron of the cesium atom is in the  $6s$  orbital,

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

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

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

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,

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

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  $r_{\text{outer}}^{hl}$  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  $r_{\text{outer}}^{hl}$ ? ♠ Why are the distances between the zeros smallest for small  $r$ ?

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

The difference between the *binding energies* of the two  $6s$  states is even bigger: For the hydrogenlike atom,  $-E^{hl}$  is more than 1 keV, while  $-E^{Cs}$  in reality is of the order of 5 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  $-E^{Cs} \sim 5 \text{ eV} > 0$ ):

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

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 further out than the corresponding zeros of  $u_{60}^{hl}$ . ♠ What must we then expect (qualitatively) when comparing the outer turning radius  $r_{\text{outer}}^{Cs}$  with  $r_{\text{outer}}^{hl}$ , and comparing  $E^{Cs}$  with  $E^{hl}$ ?

### Problem 4 (Counts 25%)

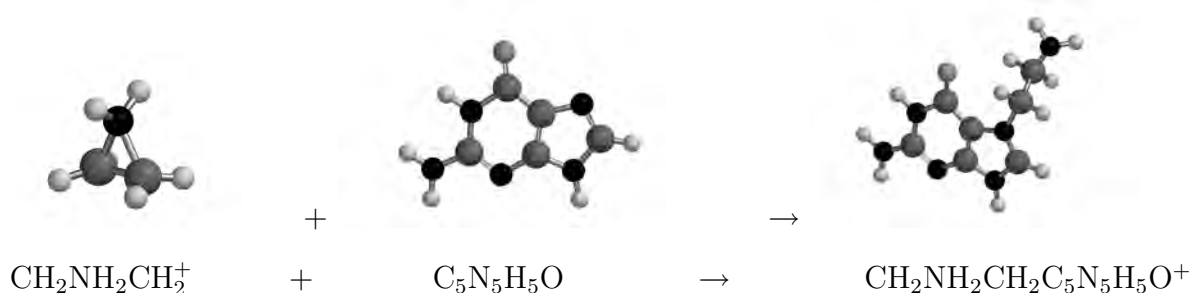
*Introduction (not really necessary for solving the problems):*

The poisonous *mustard gas*  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$  is, by substitution of the S atom with NR (where  $\text{R} = \text{H}, \text{CH}_3$ , 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  $\text{R} = \text{CH}_3$ ) when a chloride ion  $\text{Cl}^-$  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  $\text{CH}_3$  and  $\text{CH}_2\text{CH}_2\text{Cl}$  with two H atoms (see figure below, right), in order to reduce the computational time.



Hence, the reaction becomes:



(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,

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,
- $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,
- $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

♠ How many electrons are there in, respectively,

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

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,

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

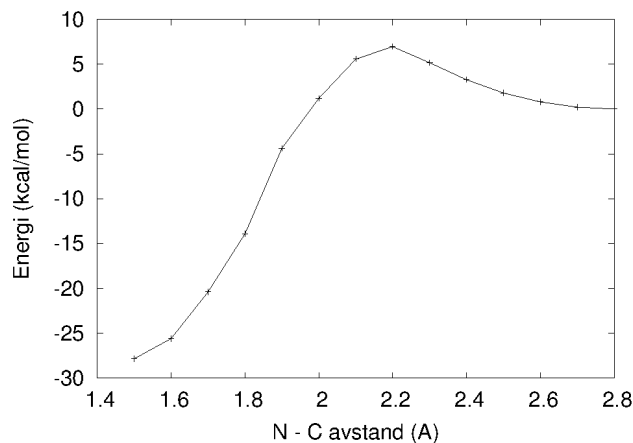
(Remember the Pauli principle!)

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

- $\text{CH}_2\text{NH}_2\text{CH}_2^+$ ,     •  $\text{C}_5\text{N}_5\text{H}_5\text{O}$ ,     •  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$  ?

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  $\text{CH}_2\text{NH}_2\text{CH}_2^+$  lasts for one second, how long time will a computation then roughly last for  $\text{CH}_2\text{NH}_2\text{CH}_2\text{C}_5\text{N}_5\text{H}_5\text{O}^+$ ?

Our computations on the above described chemical reaction, where we change the distance between the N atom in guanine and the C atom in  $\text{CH}_2\text{NH}_2\text{CH}_2^+$  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  $\exp(-E_a/k_B T)$  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,  $pV = Nk_B T$ , calculate the volume per molecule (assuming a normal pressure  $p$ ), estimate thus a mean free path between two collisions for a given molecule, and hence an average time  $\tau$  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**,  $V(x) = \frac{1}{2}kx^2$

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

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

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

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

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

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

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

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

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

**Hydrogenlike system**

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

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

**Angular functions**

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

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

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

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

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

## Ehrenfest's theorem

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

## Some constants

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

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

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

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

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

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

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

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

$$1 \text{ \AA} = 10^{-10} \text{ m}.$$

## Some formulae

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

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

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