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# Exam in TFY4205 Quantum Mechanics

25. May 2005
9:00–13:00

Allowed help: Alternativ C
Approved Calculator.
K. Rottman: *Matematische Formelsammlung*
Barnett and Cronin: *Mathematical formulae*

***Fundamental constants, useful relations and tips are given at the end of the exam.***

This problem set consists of 9 pages.

## Problem 1. Electronic transitions in one-dimensional molecules

Consider the chain polymer in the figure below.

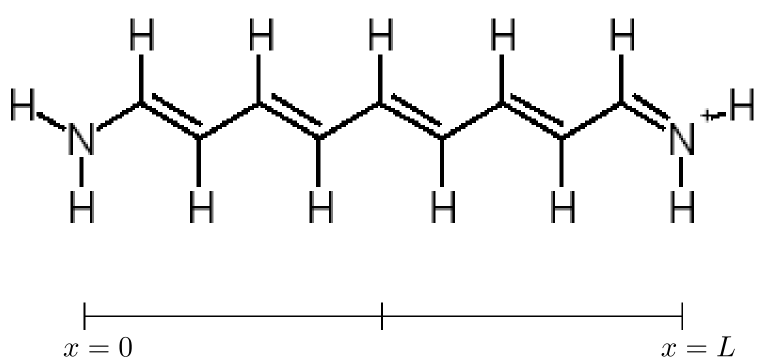


Figure 1: *A chain polymer. Carbon atoms at the bond connections are not plotted for clarity.*

There are 12 delocalized electrons that propagate freely in the one-dimensional chain between the nitrogen (N) atoms which act as infinite barriers. The distance between neighboring carbon atoms is $l_{C-C} = 1.40\text{Å}$ and between carbon and nitrogen is $l_{C-N} = 1.34\text{Å}$.

**a)** The spin-1/2 delocalized electrons in the chain do not interact but they obey the ***Pauli principle***. Neglect the small angles between the bonds, what is the wavelength of the first photon (smallest energy) that the chain may absorb?

**Solution:** The electrons are non-interacting and moves freely in the one-dimensional wire, i.e. each electron can be modeled as a single particle in a one dimensional box with length $L = 8l_{C-C} + 2l_{C-N} = 1.39nm$ with infinite barriers at $x = 0$ and $x = L$. The stationary Schrödinger equation for the one-electron problem is then given by the kinetic energy only

$$-\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \tag{1}$$

with the boundary conditions $\psi(x \leq 0) = \psi(x \geq L) = 0$. The general solution for Eq.(1) is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{2}$$

where $A$ and $B$ are integration constants and $k = \sqrt{2m_eE/\hbar^2}$. The boundary condition $\psi(x) = 0$ leads to $A = -B$ and thus

$$\psi(x) = C\sin(kx) \tag{3}$$

where $C = 2iA$. The boundary condition $\psi(L) = 0$ quantize the energy by forcing $\sin(kL) = 0$ and thereby $k = \pi n/L$. Here, $n = 1, 2, 3....$ In terms of energy

$$E = \frac{\hbar^2k^2}{2m_e} = \frac{\hbar^2\pi^2n^2}{2m_eL^2}. \tag{4}$$

To determine $C$, we can use normalization of the wavefunction

$$\int_0^L dx\ |\psi(x)|^2 = \int_0^L dx\ |C|^2\ \sin^2(\pi nx/L) = 1 \tag{5}$$

$$\rightarrow C = \sqrt{\frac{2}{L}} \tag{6}$$

The 12 electrons (fermions with spin-1/2) obey the Pauli principle, i.e they can not share the same state. There are two states each energy level, due to the electron spins. Thus all states up to energy level 6 are occupied. The photon with the lowest energy that can be absorbed by the system (at low temperature) has the energy

$$E_{photon} = E_7 - E_6 = \frac{\hbar^2\pi^2}{2m_eL^2}(7^2 - 6^2) \simeq 4.11 \times 10^{-19}J \tag{7}$$

with the corresponding photon wavelength

$$\boxed{\lambda = \frac{hc}{E_{photon}} \simeq 484\ nm}$$

i.e. violet light.

**b)** Substituting the hydrogen atom in the middle ($x = L/2$) with another atom or group may perturb the potential of the chain. Assume that the weak perturbing potential is given by

$$V(x) = \quad V_0 \qquad |x - \frac{L}{2}| \leq x_0 \tag{8}$$

$$0 \qquad |x - \frac{L}{2}| > x_0. \tag{9}$$

Here, $V_0 = 10^{-19}J$ and $x_0 = L/4$. Find the new sixth and seventh energy level using first order perturbation theory.

**Solution:** The new energy for level $n$ is, to the first order perturbation, given by

$$E_n = E_n^0 + \langle \psi_n^{old} | V(x) | \psi_n^{old} \rangle \tag{10}$$

where the superscript $^0$ denotes the unperturbed problem. Thus,

$$\begin{aligned}
E_n &= E_n^0 + \int_{L/4}^{3L/4} dx\ V_0 \frac{2}{L} \sin^2(\frac{n\pi x}{L}) &(11)\\
&= E_n^0 + \frac{2V_0}{\pi n} \int_{n\pi/4}^{n\pi 3/4} du\ \sin^2(u) &(12)\\
&= E_n^0 + \frac{2V_0}{\pi n} [\frac{u}{2} - \frac{1}{2} \sin(u)\cos(u)]_{n\pi/4}^{3n\pi/4} &(13)\\
&= E_n^0 + \frac{V_0}{2} + \frac{V_0}{\pi n} [\sin(\frac{n\pi}{4})\cos(\frac{n\pi}{4}) - \sin(\frac{3n\pi}{4})\cos(\frac{3n\pi}{4})] &(14)\\
&= E_n^0 + \frac{V_0}{2} \qquad \forall n = 2, 4, 6, 8... &(15)\\
&= E_n^0 + \frac{V_0}{2} + \frac{V_0}{\pi n} \qquad \forall n = 1, 5, 9, 13... &(16)\\
&= E_n^0 + \frac{V_0}{2} - \frac{V_0}{\pi n} \qquad \forall n = 3, 7, 11, 15... &(17)
\end{aligned}$$

where we have used the substitution $u = n\pi x/L$. For $n = 6$

$$\begin{aligned}
E_6 &= \frac{\hbar^2 \pi^2 6^2}{2m_e L^2} + \frac{V_0}{2} &(18)\\
&\simeq 1.14 \times 10^{-18} J + 0.05 \times 10^{-18} J \simeq 1.19 \times 10^{-18} J &(19)
\end{aligned}$$

and for For $n = 7$

$$\begin{aligned}
E_7 &= \frac{\hbar^2 \pi^2 7^2}{2m_e L^2} + \frac{V_0}{2} - \frac{V_0}{7\pi} &(20)\\
&\simeq 1.548 \times 10^{-18} J + 4.55 \times 10^{-20} J \simeq 1.59 \times 10^{-18} J &(21)
\end{aligned}$$

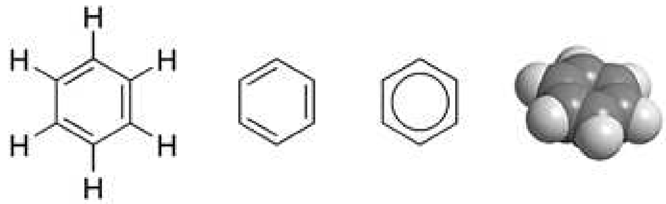

Figure 2: *Miscellaneous diagrams and a figure of the benzene molecule.*

**Problem 2. Particle in a ring**

A benzene molecule, see figure below, may be treated as an one dimensional ring with radius $R = 1.34\text{Å}$ in which six delocalized electrons can move freely around. The delocalized electrons in the ring do not interact but they obey the Pauli principle.

**a)** Find all the stationary single particle wavefunctions and their energies for the delocalized electrons.

**Solution:** The electrons are non-interacting and moves freely in the one-dimensional ring, i.e. each electron can be modeled as a single particle in a one dimensional ring with radius $R = 0.134nm$. The stationary Schrödinger equation for the one-electron problem is then to a good approximation given by the kinetic energy only

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)\psi(x, y) = E\psi(x, y) \tag{22}$$

with the constrain that the electron must moves along the ring. Since the problem is rotational invariant, it is useful to formulate it in cylindrical coordinate

$$-\frac{\hbar^2}{2m_e}\frac{1}{R^2}\frac{d^2}{d\phi}\psi(\phi) = E\psi(\phi) \tag{23}$$

where the fact of constant radius and thereby $d\psi/dr = 0$ is used. A general solution for Eq.(23) is

$$\psi(x) = Ae^{ikR\phi} + Be^{-ikR\phi}, \tag{24}$$

where $A$ and $B$ are integration constants, and $k = \sqrt{2m_eE/\hbar^2}$. In contrast to the particle in a 1D box, here the $\pm$ solutions are independent from each other. Thus,

$$\psi(x) = Ae^{\pm ikR\phi}, \tag{25}$$

Normalization

$$\int_0^{2\pi} d\phi\ A^2\ |\psi|^2 \ = \ 1 \tag{26}$$

$$\rightarrow A \ = \ \sqrt{\frac{1}{2\pi}} \tag{27}$$

The boundary condition $\psi(\phi) = \psi(\phi + 2\pi)$, coming from the demand that the wave-function is single valued, leads to energy quantization

$$\begin{aligned} \psi(\phi) &= \psi(\phi + 2\pi) && (28)\\ e^{\pm ikR\phi} &= e^{\pm ikR(\phi+2\pi)} && (29)\\ 1 &= e^{\pm ikR2\pi} && (30) \end{aligned}$$

This leads to $kR = n$, where $n = 0, 1, 2, 3...$ and consequently

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2 n^2}{2m_e R^2}. \tag{31}$$

Giving the final wavefunction

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm in\phi} \tag{32}$$

**b)** Find the angular momentum for the wavefunctions in a).

**Solution:** The angular momentum operator is

$$\vec{L} = \vec{r} \times \vec{p} \tag{33}$$

Since the electron moves in a ring in the xy-plane only $L_z$ is none zero. In spherical coordinate

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \tag{34}$$

giving the eigenvalues

$$\begin{aligned} L_z\ \psi &= \frac{\hbar}{i} \frac{\partial}{\partial \phi}\ \psi && (35)\\ &= \pm n\hbar\ \psi && (36) \end{aligned}$$

Note that the total angular momentum $L^2 = L_x^2 + L_y^2 + L_z^2 = L_z^2$, will in this case gives the eigenvalues

$$L^2\ \psi = L_z^2\ \psi = \hbar^2 n^2\ \psi \tag{37}$$

an not the standard $l(l + 1)$ as in 3-dimensions.

**Problem 3. Addition of spin**

Assume that $\vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3$ is the total spin of a collection of three electrons. What are the possible eigenvalues of $S^2$?

**Solution:** The eigenvalues of $\vec{S}_A = \vec{S}_1 + \vec{S}_2$ are $S_A = 0, 1$. The eigenvalues of $\vec{S} = \vec{S}_A + \vec{S}_3$ are therefore $S = 1/2, 3/2$.

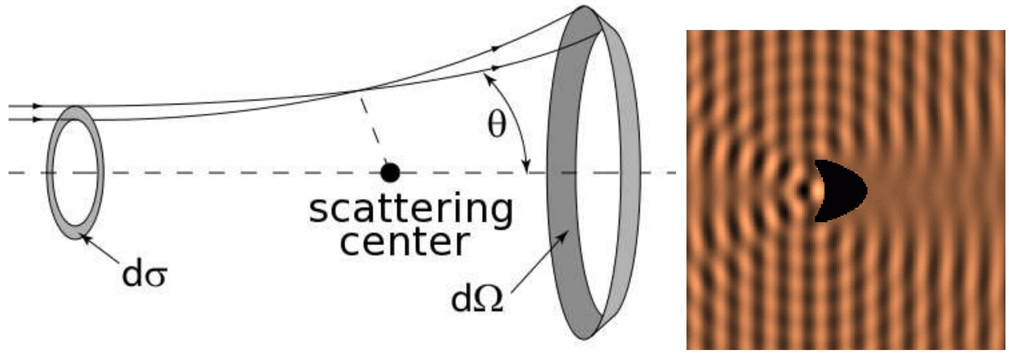


Figure 3: *Left: schematic figure of the scattering problem. Right: scattering of a plane wave against a sickle shaped potential. Note that the Yukawa-Coulomb potential has spherical symmetry.*

**Problem 4. Scattering problem**
Consider a three-dimensional, stationary scattering problem of an electron with a large momentum $\vec{p} = \hbar\vec{k}$ hitting an aluminium atom with a Yukawa-Coulomb potential $V(\vec{r}) = U_0 e^{-\alpha r}/r$. Here, $U_0 = -13e^2/4\pi\epsilon_0$ and $1/\alpha$ is a screening length.

**a)** Formulate the problem in terms of a stationary Schrödinger equation and state the boundary conditions. Propose a form of the wavefunction that is valid at distances far away from the scattering center.

**Solution:** The Schrödinger equation for the problem is

$$[-\frac{\hbar^2}{2m_e}\nabla^2 + V(r)]\ \psi(\vec{r}) = E\psi(\vec{r}) \tag{38}$$

With the boundary conditions: 1) An incoming electron described by a plane wave $e^{i\vec{k}\cdot\vec{r}}$ and 2) The scattered wave is purely outgoing. Time invariance and inelastic scattering leads to energy conservation $E = \frac{\hbar^2 k^2}{2m_e}$ which is the kinetic energy of the incoming electron.

Far away from the scattering center where the potential is approximately zero, the solutions of $-\frac{\hbar^2}{2m_e}\nabla^2\psi(\vec{r}) = E\psi(\vec{r})$ should describe free propagating waves . In 3D the free propagating waves can take different forms depend on the initial conditions. For our problem the incoming electron dictates a plane wave ($e^{i\vec{k}\cdot\vec{r}}$) solution and the "point" scattering propose a spherical wave ($e^{ikr}/r$) solution. The large $r$ solution for Eq. (38) is then

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + f(\theta,\phi)e^{ikr}/r \tag{39}$$

where the angular function $f(\theta,\phi)$ depend on the details of the scattering process.

**b)** A formal solution of the wavefunction for the scattering problem given in a) is

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int d^3r'\ G(\vec{r}-\vec{r}')\ \frac{2m}{\hbar^2}V(\vec{r}')\ \psi(\vec{r}') \tag{40}$$

$$G(\vec{r}-\vec{r}') = -\frac{e^{ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|} \tag{41}$$

where $\psi_0(\vec{r})$ is the solution of the problem without the scattering potential. Use the *first order Born-approximation* and the large $r$ approximation: i.e. $k|\vec{r}-\vec{r}'| \approx kr - \vec{k}' \cdot \vec{r}'$, $\vec{k}' = k\vec{r}/r$ and $1/|\vec{r}-\vec{r}'| \approx 1/r$ to find the differential scattering cross section for the electron expressed by fundamental constants, $\alpha$ and $|\vec{q}| = |\vec{k}' - \vec{k}| = 2k\sin(\theta/2)$.

**Solution:** To the first order Born approximation

$$\psi(\vec{r}) \simeq \psi_0(\vec{r}) + \int d^3r'\ G(\vec{r}-\vec{r}')\ \frac{2m_e}{\hbar^2} V(\vec{r}')\ \psi_0(\vec{r}') \tag{42}$$

$$= e^{i\vec{k}\cdot\vec{r}} + \int d^3r'\ G(\vec{r}-\vec{r}')\ \frac{2m_e}{\hbar^2} V(\vec{r}')\ e^{i\vec{k}\cdot\vec{r}'} \tag{43}$$

$$= e^{i\vec{k}\cdot\vec{r}} + \frac{-2m_e}{\hbar^2 4\pi} \int d^3r'\ \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\ V(\vec{r}')\ e^{i\vec{k}\cdot\vec{r}'} \tag{44}$$

$$\tag{45}$$

where we have used $\psi_0 = e^{i\vec{k}\cdot\vec{r}}$. Using the and the large $r$ approximation, we find

$$\psi(\vec{r}) \simeq e^{i\vec{k}\cdot\vec{r}} + \frac{-m_e}{\hbar^2 2\pi} \frac{e^{ikr}}{r} \int d^3r'\ e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'}\ V(\vec{r}') \tag{46}$$

Giving the scattering amplitude

$$f(\theta,\phi) = \frac{-m_e}{\hbar^2 2\pi} \frac{e^{ikr}}{r} \int d^3r'\ e^{-i\vec{q}\cdot\vec{r}'}\ V(\vec{r}') \tag{47}$$

where $\vec{q} = \vec{k}' - \vec{k}$ and $q = 2k\sin(\theta/2)$. Integrating over the angles

$$f(\theta,\phi) = \frac{-m_e}{\hbar^2 2\pi} \int_0^{\pi} d\theta'\ \sin(\theta') \int_0^{2\pi} d\phi' \int_0^{\infty} dr'\ e^{-iqr'\cos\theta'}\ V(\vec{r}') \tag{48}$$

$$= \frac{-2m_e}{\hbar^2 q} \frac{13e^2}{4\pi\epsilon_0} \frac{q}{\alpha^2 + q^2} \tag{49}$$

The differential scattering cross section is

$$\frac{d\sigma}{d\Omega} = |f(\theta,\phi)|^2 \tag{50}$$

***Useful fundamental constants and relations:***

**a) Fundamental constants:**

Elementary charge $e = 1.60 \times 10^{-19} C$
Electron mass $m_e = 9.11 \times 10^{-31} kg$
Planck constant $h = 6.63 \times 10^{-34} Js$
Velocity of light $c = 3.00 \times 10^{8} m/s$
Permitivity $\epsilon_0 = 8.85 \times 10^{-12} C^2/Nm^2$

**b)** The differential equation

$$\frac{d^2}{dx^2}f(x) + k^2 f(x) = 0 \tag{51}$$

$$\tag{52}$$

has the general solution

$$f(x) = Ae^{ikx} + Be^{-ikx} \tag{53}$$

**c)** Useful integral #1

$$\int dx\ \sin^2(x) = \frac{1}{2}x - \frac{1}{2}\sin(x)\cos(x) \tag{54}$$

**d)** Laplace operator in cylindrical coordinates $(\rho, \phi, z)$

$$x = \rho\cos\phi \tag{55}$$

$$y = \rho\sin\phi \tag{56}$$

$$z = z \tag{57}$$

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho\frac{\partial f}{\partial\rho}) + \frac{1}{\rho^2}\frac{\partial^2 f}{\partial\phi^2} + \frac{\partial^2 f}{\partial z^2} \tag{58}$$

**e)** Derivative operator in spherical coordinate $(r, \theta, \phi)$

$$x = r\sin\theta\cos\phi \tag{59}$$

$$y = r\sin\theta\sin\phi \tag{60}$$

$$z = r\cos\theta \tag{61}$$

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{62}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi} \tag{63}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta} \tag{64}$$

**f)** Useful Jacobians

$$\int d^3r = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\sin\theta \int_0^{\infty} dr\ r^2 \tag{65}$$

$$= \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \int_0^{\infty} dr\ r^2 \tag{66}$$

$$\tag{67}$$

**g)** A vector relation

$$\vec{q} = \vec{k}' - \vec{k} \tag{68}$$

if $k = k'$ then

$$q = 2k\sin(\theta/2) \tag{69}$$

where $\theta$ is the angle between $\vec{k}$ and $\vec{k}'$.

**h)** Useful integral #2

$$\int_0^\infty dr\ e^{-\alpha r} \sin(qr) = \frac{q}{\alpha^2 + q^2} \tag{70}$$