Exam
Quantum Engineering (FKA132), Chalmers
2015-10-27

Time and place: 14:00-18:00 on October 27, 2015, Campus Johanneberg.
Examinator: Elsebeth Schröder (tel 031 772 8424).
Allowed references: Dictionaries, Beta, Physics Handbook, one handwritten paper of size A4 (both sides) with own notes, and a Chalmers-approved calculator. Correct solution of each problem gives 6 points. 15 points are needed to pass.
Motivate your answers, answers lacking reasonable motivation will not yield full credit.

Problem 1. (One point per question)
a) Explain what is a two-level system and give examples of (three to four) physical systems that can at least approximately be considered two-level systems.

b) Show by explicit use of the definitions of commutators and anticommutators that for operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ the following applies:
$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} = \hat{A}\{\hat{B}, \hat{C}\} - \{\hat{A}, \hat{C}\}\hat{B}$

c) Which of the following are Hermitian operators? $\hat{p}\hat{x}$, $\hat{x}\hat{p} + \hat{p}\hat{x}$, $\hat{H}\hat{x}$.

d) Two observables are represented by the operators $\hat{A}$ and $\hat{B}$. What does the relation $[\hat{A}, \hat{B}] = 0$ imply?

e) Define the concept "electronegativity"

f) Explain what an orbital (atomic or molecular) is.

Problem 2.
For an electron in a magnetic field $\mathbf{B} = B_0(1, 0, 0)$ the Hamiltonian for the spin part is given by

$$\hat{H} = -\frac{1}{\mu_0}\boldsymbol{\mu} \cdot \mathbf{B}\,, \qquad \boldsymbol{\mu} = -\frac{g\mu_B}{2}\boldsymbol{\sigma} \tag{1}$$

where $g \approx 2.00$ is the Landé factor, $\mu_B = e\hbar/(2m_e c)$ is the Bohr magneton, $\boldsymbol{\sigma}$ the Pauli spin matrices, and μ_0 the magnetic permability. The vector $(1, 0, 0)$ is the unit vector in the x-direction.

a) Calculate the eigenvalues and the (normalized) eigenvectors of the hamiltonian $\hat{H}$.

b) At time $t = 0$ the electron is in its spin-up state, relative to the z-axis. What are the probabilities of measuring each of the energy values obtained in question (a)?

c) Describe the time evolution of the spin state of the electron at $t > 0$, i.e., the spin wavefunction as a function of time, $\chi(t)$.

d) Calculate the probabilities of finding the electron in the spin-up state, $P_\uparrow(t)$, and the spin-down state, $P_\downarrow(t)$, as a function of time $t > 0$.

Problem 3.
The one-dimensional harmonic oscillator is given by the potential energy operator $\hat{V}_0(x) = \frac{1}{2}m\omega^2\hat{x}^2$. Oscillations in nature are seldom clean harmonic oscillations, there will often be some degree of anharmonicity in the oscillations. A perturbation that conserves the symmetry of the harmonic oscillator around $x = 0$ is $\hat{H}' = \lambda m^2\omega^3\hat{x}^4/\hbar$. The total hamiltonian becomes $\hat{H} = \hat{H}_0 + \hat{H}'$.

a) Write the perturbation $\hat{H}'$ in terms of the annihilation and creation operators $\hat{b}$ and $\hat{b}\dagger$; $\hat{b} = (m\omega\hat{x} + i\hat{p}_x)/\sqrt{2\hbar m\omega}$.

b) Using perturbation theory, find the first order change to the ground state energy.

c) What are the first-order changes to the energies of the excited states? (This question will give you a number of nonvanishing terms to keep track of—don't give up)

d) Using perturbation theory, show that the second order change to the ground state energy is $-(21/8)\lambda^2\hbar\omega$.

Problem 4.
Last year an article was published in Physical Review Letters, with the following abstract (here given only in parts)

> "One of the enduring challenges in graphene research and applications is the extreme sensitivity of its charge carriers to external perturbations, especially those introduced by the substrate. The best available substrates to date, graphite and hexagonal boron nitride (h-BN), still pose limitations: graphite being metallic does not allow gating, while both h-BN and graphite, having lattice structures closely matched to that of graphene, may cause significant band structure reconstruction. Here we show that the atomically smooth surface of exfoliated MoS_2 provides access to the intrinsic electronic structure of graphene without these drawbacks. Using scanning tunneling microscopy [...] we find that graphene on MoS_2 is ultraflat [...] MoS_2 substrates thus provide unique opportunities to access the intrinsic electronic properties of graphene [...]"

from *MoS_2: Choice Substrate for Accessing and Tuning the Electronic Properties of Graphene*, by Chih-Pin Lu, Guohong Li, K. Watanabe, T. Taniguchi, and Eva Y. Andrei, Physical Review Letters **113**, 156804 (2014).

In order to find that graphene is so exceptionally smooth on MoS_2 the authors thus used scanning tunneling microscopy (STM), moving a metallic tip across the surface.

a) With a few sentences and a sketch, describe how an STM works and how it is relevant for this course in Quantum Engineering. What would be an appropriate distance between the metallic tip and the surface (roughly)? Use Figure 1 in your arguments for your estimate.

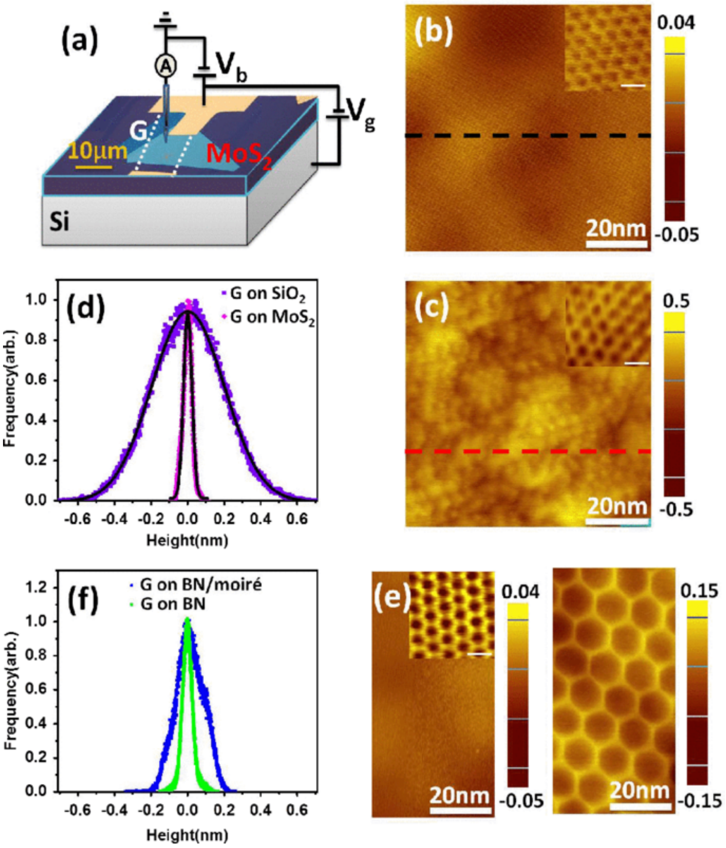


Figure 1: From the original paper: "(a) Schematic of STS [Scanning tunneling spectroscopy] measurement setup showing the graphene sample (G) and MoS$_2$ substrate. The sample bias V_b is applied between the STM tip and the sample. The edge of the graphene flake is marked by dashed lines. The back gate voltage V_g is applied between the Si substrate and the top electrode. (b),(c) STM topography of graphene on MoS$_2$ and on chlorinated SiO$_2$, respectively. (d) Height histograms of the topography images in (b) and (c). (e) Same as (b) for graphene on h-BN with (right) and without (left) Moiré pattern. (f) Height histograms of the topography images in (e). Image area 80×80 nm (b),(c) and 40×80 nm (e). Insets in (b),(c), and (e) represent zoom-in images with scale bar 0.3 nm. STS parameters: set point current $I = 20$ pA at $V_b = 0.4$ V."

b) A particle in an infinite one-dimensional square well of width a has the following wavefunction at time $t = 0$

$$\psi(x, t = 0) = \sqrt{\frac{2}{9a}} \left(\sin\left\{\frac{\pi x}{a}\right\} + \sqrt{3} \sin\left\{\frac{3\pi x}{a}\right\} + \sqrt{5} \sin\left\{\frac{5\pi x}{a}\right\} \right) \tag{2}$$

Which values of the energy would be the possible outcomes in a measurement at $t = 0$?

c) What are the probabilities of measuring each of the energy values in (b)?

d) What is the wavefunction above (question (b)) at a later time t'? Does this describe a stationary state? (Argue for your answer)

e) The one-dimensional square well allows for stationary states with a range of energies E_n^{1D}. Take the energy of the fourth excited state and call it ϵ^{1D}. Now imagine a THREE-dimensional infinite square well with width a in all three dimensions (you can think of this as a simple model of a quantum dot). How many states in the 3D square well exist that have an energy *less than or equal to* the energy ϵ^{1D}?

f) Write down the ground state wavefunction (in a x-y-z coordinate system) of the 3D square well.

Problem 5.

Aromatic compounds, for example thiophenol, often form well-ordered self-assembled monolayers on metals exhibiting a typical structure called a herringbone pattern, see Figure 2(a). One major driving force for the formation of this particular structure is the favorable intermolecular interaction achieved for packing geometries similar to the one illustrated in the Figure 2(b) and (e).

a) Describe the difference between the σ-skeleton and the π-system in benzene in terms of atomic orbital overlap. (2 points)

b) Describe the origin of the intermolecular interaction between two benzene molecules and explain why the packing geometry resulting in the herringbone structure is particularly favorable. (4 points)

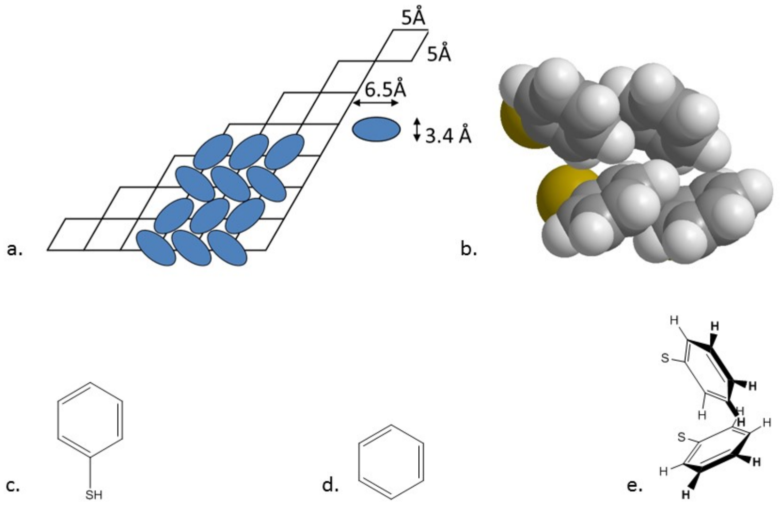


Figure 2: (a) Schematic representation of the herringbone pattern of thiophenol on an Au(111) surface. The grid represents the gold surface and the ellipses the edge view of the benzene ring of the thiophenols. (b) The herringbone packing geometry (gold surface omitted). The large atoms furthest away are the sulfur atoms bond to the surface. (c) Thiophenol. (d) Benzene. (e) Perspective drawing of the herringbone packing geometry.

END OF DOCUMENT

Exam FKA132 Chalmers 2015-10-27

Sketch of answers

1\. a) Two-level systems, see BAND 6.1

b) $[AB, C] = ABC - CAB$ (from definition of commutator)

$$A[B,C] + [A,C]B = ABC - ACB + ACB - CAB = ABC - CAB$$

$$A\{B,C\} - \{A,C\}B = ABC + ACB - ACB - CAB = ABC - CAB$$

c) $\hat{x}, \hat{p}, \hat{H}$ hermitian (can prove that, too)

$\hat{p}\hat{x}$ hermitian?

$$\int \psi^* \hat{p}\hat{x}\psi\, dx \overset{\hat{x}=\hat{x}^+,\ \hat{p}=\hat{p}^+}{\overset{\downarrow}{=}} \int \psi^* \hat{p}^+\hat{x}^+ \psi\, dx = \int (\hat{x}\hat{p}\psi)^* \psi\, dx$$

$$\neq \int (px\psi)^* \psi\, dx$$

because $[p, x] = -i\hbar \neq 0$. Not hermitian

$\hat{p}\hat{x} + \hat{x}\hat{p}$? From above $(\hat{x}\hat{p})^+ = \hat{p}\hat{x}$ and similarly $(\hat{p}\hat{x})^+ = \hat{x}\hat{p}$

Thus $(\hat{p}\hat{x} + \hat{x}\hat{p})^+ = (\hat{p}\hat{x})^+ + (\hat{x}\hat{p})^+ = \hat{p}\hat{x} + \hat{x}\hat{p}$

Hermitian!

$\hat{H}\hat{x}$? We know $[\hat{H}, \hat{x}] = 0$ (or can prove).

$$\int (\hat{H}\hat{x}\psi)^* \psi\, dx = \int \psi^* \hat{x}^+\hat{H}^+ \psi\, dx = \int \psi^* \hat{x}\hat{H}\psi\, dx$$

$$\underset{[\hat{H},\hat{x}]=0}{\underset{\nearrow}{=}} \int \psi^* \hat{H}\hat{x}\psi\, dx$$

so $(\hat{H}\hat{x})^+ = \hat{H}\hat{x}$ Hermitian

d) $\hat{A}, \hat{B}$ observables, $[\hat{A}, \hat{B}] = 0$: $\hat{A}$ and $\hat{B}$ share the same eigenvectors, so can be measured simultaneously

2) $\vec{B} = B_0\,(1, 0, 0)$

$$\hat{H} = -\frac{1}{\mu_0}\,\vec{\mu}\cdot\vec{B} = \frac{g}{2}\,\frac{\mu_B}{\mu_0}\,\vec{\sigma}\cdot\vec{B} \qquad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$= \frac{g}{2}\,\frac{\mu_B}{\mu_0}\,B_0\,\sigma_x$$

a) Eigenvalues and -vectors for $\hat{H}$: concentrate on σ_x first.

$\sigma_x\,|\lambda\rangle = \lambda\,|\lambda\rangle$ solutions if $\det\left(\sigma_x - \lambda \mathbb{1}\right) = 0$

$$\begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = \lambda^2 - 1 = 0 \quad \therefore \lambda = \pm 1$$ (real because $\hat{H}$ is observable)

$$|\lambda\rangle \sim \begin{pmatrix} a \\ b \end{pmatrix}$$

$\lambda = 1$:
$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad \therefore \quad a = b$$

$$|\lambda = 1\rangle \sim \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$\lambda = -1$
$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad \therefore \quad a = -b$$

$$|\lambda = -1\rangle \sim \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Eigenvalues and -vectors for $\hat{H}$:

$(\lambda = 1)$ $\quad E_1 = \frac{g}{2}\,\frac{\mu_B}{\mu_0}\,B_0$, $\quad |\lambda = 1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \sim \chi_+$

$(\lambda = -1)$ $\quad E_{-1} = -\frac{g}{2}\,\frac{\mu_B}{\mu_0}\,B_0$, $\quad |\lambda = -1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \sim \chi_-$

b) spin-up $|\uparrow\rangle \sim \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$\langle\uparrow|\lambda=1\rangle = \frac{1}{\sqrt{2}}(1 \;\; 0)\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}, \quad P_1 = |\langle\uparrow|\lambda=1\rangle|^2 = \frac{1}{2}$$

$$\langle\uparrow|\lambda=-1\rangle = \frac{1}{\sqrt{2}}(1\;0)\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}, \quad P_{-1} = |\langle\uparrow|\lambda=-1\rangle|^2 = \frac{1}{2}$$

c) Time evolution

$$\chi(t) = c_+\,\chi_+\,e^{\frac{-iE_1 t}{\hbar}} + c_-\,\chi_-\,e^{\frac{-iE_{-1} t}{\hbar}}.$$

At $t=0$: $\chi(t=0) = c_+\chi_+ + c_-\chi_-$
$= \frac{1}{\sqrt{2}}\chi_+ + \frac{1}{\sqrt{2}}\chi_-$

(2c cont'd)

$$\chi(t) = \frac{1}{\sqrt{2}}\chi_+ e^{-i\varepsilon t/\hbar} + \frac{1}{\sqrt{2}}\chi_- e^{+i\varepsilon t/\hbar}$$

$$\varepsilon = \frac{g}{2}\frac{\mu_B}{\mu_0} B_0$$

d) spin-up $\chi_\uparrow \sim \begin{pmatrix}1\\0\end{pmatrix}$

$$\langle\chi_\uparrow|\chi(t)\rangle = \left(\frac{1}{\sqrt{2}}\right)^2\left(e^{-i\varepsilon t/\hbar} + e^{i\varepsilon t/\hbar}\right) = \cos\left(\frac{\varepsilon t}{\hbar}\right)$$

$$P_\uparrow = |\langle\chi_\uparrow|\chi(t)\rangle|^2 = \cos^2\left(\frac{\varepsilon t}{\hbar}\right)$$

spin-down $\chi_\downarrow \sim \begin{pmatrix}0\\1\end{pmatrix}$

$$\langle\chi_\downarrow|\chi(t)\rangle = \left(\frac{1}{\sqrt{2}}\right)^2\left(e^{-i\varepsilon t/\hbar} - e^{i\varepsilon t/\hbar}\right) = -i\sin(\varepsilon t/\hbar)$$

$$P_\downarrow = |\langle\chi_\downarrow|\chi(t)\rangle|^2 = \sin^2(\varepsilon t/\hbar)$$

Check: $P_\uparrow + P_\downarrow = \cos^2(\varepsilon t/\hbar) + \sin^2(\varepsilon t/\hbar) = 1$ ok.

3)

$$\hat{H}' = \lambda m^2\omega^3 x^4/\hbar \quad , \quad b = (m\omega x + ip_x)/\sqrt{2\hbar m\omega}$$

a) $b + b^\dagger = (2\hbar m\omega)^{-1/2}(2m\omega x + ip_x - ip_x)$

$\therefore \quad x = (b + b^\dagger)\sqrt{\dfrac{\hbar}{2m\omega}}$

$\hat{H}' = \lambda \dfrac{m^2\omega^3}{\hbar}(b+b^\dagger)^4\left(\dfrac{\hbar}{2m\omega}\right)^2 = \dfrac{\lambda}{4}\hbar\omega\,(b+b^\dagger)^4$

b) $E_0^{(1)} = \langle 0|H'|0\rangle = \dfrac{\lambda}{4}\hbar\omega \;\langle 0|(b+b^\dagger)^4|0\rangle$

$(b+b^\dagger)^4$ gives a series of terms. $\langle n|\ldots|n\rangle$ is only nonzero if there is an equal number of annihilation and creation operators, i.e. two $b^\dagger$ and two b. $\ldots|0\rangle$ is only nonzero if the rightmost operator is $b^\dagger$, and $\langle 0|\ldots$ requires the leftmost operator to be b. This leaves two possibly nonzero terms: $\langle 0|bbb^\dagger b^\dagger|0\rangle$ and $\langle 0|bb^\dagger bb^\dagger|0\rangle$.

$b|n\rangle = \sqrt{n}\,|n-1\rangle$

$b^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$

Thus $\langle 0|bbb^\dagger b^\dagger|0\rangle = 2$, $\langle 0|bb^\dagger bb^\dagger|0\rangle = 1$

$E_0^{(1)} = \dfrac{\lambda}{4}\hbar\omega\,(2+1) = \dfrac{3\lambda\hbar\omega}{4}$

c) $E_n^{(1)} = \langle n|H'|n\rangle$. $n > 0$ because this is an excited state.

First assume $n \geq 2$ to make life easier.

Then these terms are nonzero: (sorry, I changed to use $a, a^\dagger$)

$\langle n|aaa^\dagger a^\dagger|n\rangle = \sqrt{n+1}\sqrt{n+2}\sqrt{n+2}\sqrt{n+1} = (n+1)(n+2)$

$\langle n|aa^\dagger aa^\dagger|n\rangle = \sqrt{n+1}\sqrt{n+1}\sqrt{n+1}\sqrt{n+1} = (n+1)^2$

$\langle n|a^\dagger aaa^\dagger|n\rangle = \sqrt{n+1}\sqrt{n+1}\sqrt{n}\sqrt{n} = (n+1)n$

$\langle n|aa^\dagger a^\dagger a|n\rangle = \sqrt{n}\sqrt{n}\sqrt{n+1}\sqrt{n+1} = (n+1)n$

$\langle n|a^\dagger aa^\dagger a|n\rangle = \sqrt{n}\sqrt{n}\sqrt{n}\sqrt{n} = n^2$

$\langle n|a^\dagger a^\dagger aa|n\rangle = \sqrt{n}\sqrt{n-1}\sqrt{n-1}\sqrt{n} = n(n-1)$

Sum $= 6(n^2 + n + \tfrac{1}{2})$

$E_n^{(1)} = \dfrac{\lambda}{4}\hbar\omega\, 6(n^2+n+\tfrac{1}{2})$ for $n \geq 2$

3c cont'd :

For $n=1$ the last term vanishes (two annihilation operators acting on $|1\rangle$, $bb\,|1\rangle = 0$). The sum of the five remaining terms is 15. But $6\,(n^2+n+\frac{1}{2}) = 15$ for $n=1$, so also $n=1$ is covered in the expression

$$E_n^{(1)} = \lambda \hbar\omega\, \frac{3}{2}\,(n^2+n+\tfrac{1}{2}) \quad , \ n \geq 1$$

Always positive! (any n)

d) $$E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle n|H'|0\rangle|^2}{E_0^{(0)} - E_n^{(0)}} \qquad \circledast$$

We need to find the nonvanishing terms in $\langle n|H'|0\rangle$.

Must have b^+ rightmost. Because $n \neq 0$ we cannot have an equal number of b^+ and b. Of interest are the terms

$\langle n|\, b^+b^+b^+b^+ |0\rangle = 1\cdot\sqrt{2}\,\sqrt{3}\,\sqrt{4}\ \langle n|4\rangle \quad = 2\sqrt{6}\,\langle n|4\rangle$

$\langle n|\, b\,b^+b^+b^+ |0\rangle = 1\cdot\sqrt{2}\,\sqrt{3}\,\sqrt{3}\ \langle n|2\rangle \quad = 3\sqrt{2}\,\langle n|2\rangle$

$\langle n|\, b^+b\,b^+b^+ |0\rangle = 1\cdot\sqrt{2}\,\sqrt{2}\,\sqrt{2}\ \langle n|2\rangle \quad = 2\sqrt{2}\,\langle n|2\rangle$

$\langle n|\, b^+b^+b\,b^+ |0\rangle = 1\cdot 1\cdot 1\,\sqrt{2}\ \langle n|2\rangle \quad = \sqrt{2}\,\langle n|2\rangle$

$\langle n|\, b\,b\,b\,b^+ |0\rangle = 0$ because $b\,(b\,b^+|0\rangle) = b\,|0\rangle = 0$

Only $n=2$ and $n=4$ in the sum $\circledast$ contribute.

$E_0^{(0)} = \frac{1}{2}\hbar\omega$, $E_2^{(0)} = \frac{5}{2}\hbar\omega$, $E_4^{(0)} = \frac{9}{2}\hbar\omega$

$$E_0^{(2)} = \left(\frac{|3\sqrt{2} + 2\sqrt{2} + \sqrt{2}|^2}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega} + \frac{|2\sqrt{6}|^2}{\frac{1}{2}\hbar\omega - \frac{9}{2}\hbar\omega} \right) \left(\lambda \frac{\hbar\omega}{4}\right)^2$$

$$= -\lambda^2 \hbar\omega\, \frac{21}{8}$$

Negative!

4 a) STM : See Band 1.1.6

Appropriate distance : If tip height kept constant then the height must be around 0.6 nm or more (see diagram (d)).

Accepted answer : order of magnitude 1 nm.

b) Compare to the steady state solutions

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{(Physics Handbook)}$$

$$E_n = n^2 \frac{\pi^2\hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots$$

to see that $n = 1, 3$ and 5 are involved in $\psi(x,t)$ given in (2)

c) Prefactors (coefficients)

$$c_1 = \frac{1}{\sqrt{9}} \qquad c_3 = \frac{1}{\sqrt{9}}\sqrt{3} \qquad c_5 = \frac{1}{\sqrt{9}}\sqrt{5}$$

$$P_1 = c_1^2 = \frac{1}{9} \qquad P_3 = c_3^2 = \frac{1}{3} \qquad P_5 = c_5^2 = \frac{5}{9}$$

Check : $P_1 + P_3 + P_5 = \frac{1}{9} + \frac{3}{9} + \frac{5}{9} = 1$ O.K.

d)

$$\psi(x,t) = \sqrt{\frac{2}{9a}} \left\{ \sin\left\{\frac{\pi x}{a}\right\} e^{-iE_1t/\hbar} + \sqrt{3}\sin\left\{\frac{3\pi x}{a}\right\} e^{-iE_3t/\hbar} + \sqrt{5}\sin\left\{\frac{5\pi x}{a}\right\} e^{-iE_5t/\hbar} \right\}$$

with $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$, $E_3 = 9\frac{\pi^2\hbar^2}{2ma^2}$, $E_5 = 25\frac{\pi^2\hbar^2}{2ma^2}$.

This is not a stationary state, it changes probability of finding E_1, E_3, E_5 (among others) with time. The $\psi_n(x)$ above in question b) are stationary.

e) Energy of fourth excited 1D state $E_5^{1D} = 25\frac{\pi^2\hbar^2}{2ma^2}$

3D energy $E_{n_x n_y n_z} = (n_x^2 + n_y^2 + n_z^2)\frac{\pi^2\hbar^2}{2ma^2}$, possible combinations of $n_x\, n_y\, n_z$ that yields $n_x^2 + n_y^2 + n_z^2 \leq 25$:

n_x	1	1	1	2	1	2	2	2	1	1	3	1
n_y	1	1	2	1	2	1	2	2	1	3	1	2
n_z	1	2	1	1	2	2	1	2	3	1	1	3
$n_x^2+n_y^2+n_z^2$	3	6	6	6	9	9	9	12	11	11	11	14

... etc totally 38 states (5 states in 1D!).

an estimate using the volume of the ball with radius 5-1 is also accepted.

f) Ground state 3D $\psi_0(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{\pi z}{a}\right)$ from factorization.

Exam questions and answers
October 27, 2015

1. Define the concept “electronegativity”.

2. Explain what an orbital (atomic or molecular) is.

3. Aromatic compounds, for example thiophenol, often form well-ordered self-assemble monolayers on metals exhibiting a typical structure called a herringbone pattern, see *Figure a*. One major driving force for the formation of this particular structure is the favorable intermolecular interaction achieved for packing geometries similar to the one illustrated in the *Figure b.* and *e*. below.

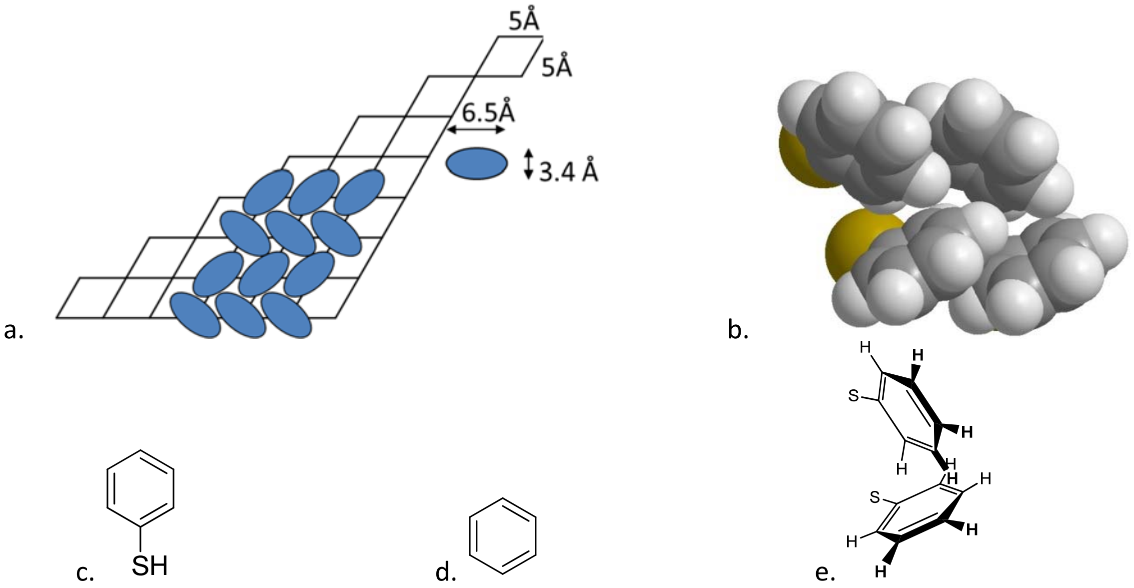


Figure. *(a) Schematic representation of the herringbone pattern of thiophenol on an Au(111) surface. The grid represents the gold surface and the ellipses the edge view of the benzene ring of the thiophenols. (b) The herringbone packing geometry (gold surface omitted). The large atoms furthest away are the sulfur atoms bond to the surface. (c) Thiophenol. (d) Benzene. (e) Perspective drawing of the herringbone packing geometry.*

   a. Describe the difference between the σ-skeleton and the π-system in benzene in terms of atomic orbital overlap. (2)
   b. Describe the origin of the intermolecular interaction between two benzene molecules and explain why the packing geometry resulting in the herringbone structure is particularly favorable. (4)

Answers to exam questions

4. Define the concept “electronegativity”.
   ***Answer**: The tendency of an atom (or group of atoms) to attract electrons from for example neighboring atoms.*

5. Explain what an orbital (atomic or molecular) is.
   ***Answer:** A wave function describing the state of a single electron in an atom or in a* molecule. *The geometrical shapes representing the eigenfunctions that satisfy Schrödinger’s equation. The stationary state of one electron.*

6. Aromatic compounds, for example thiophenol, often form well-ordered self-assemble monolayers on metals exhibiting a typical structure called a herringbone pattern, see *Figure a*. One major driving force for the formation of this particular structure is the favorable intermolecular interaction achieved for packing geometries similar to the one illustrated in the *Figure b.* and *e*. below.

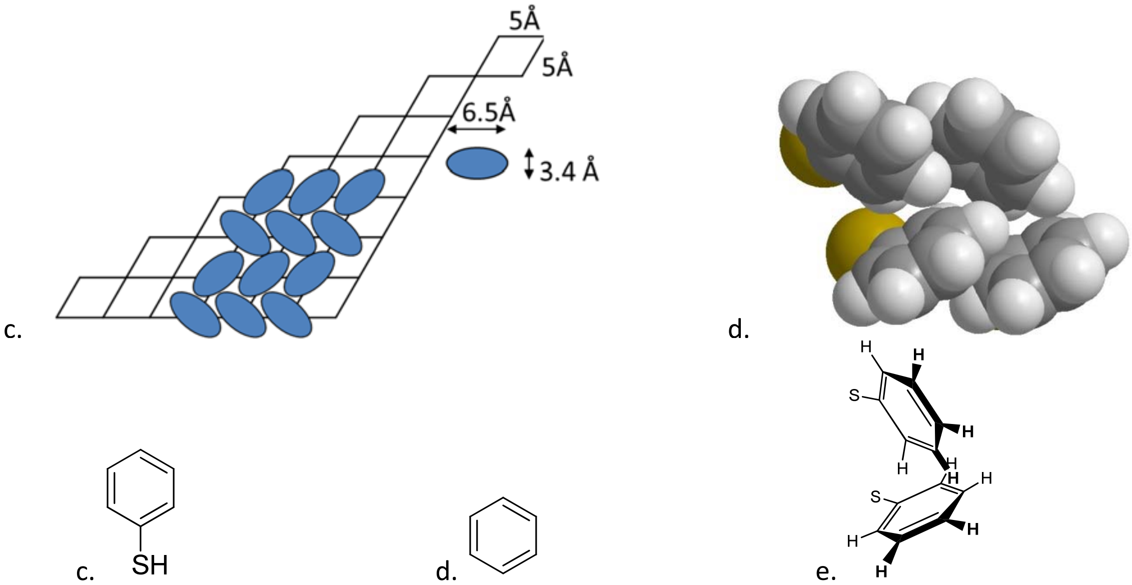
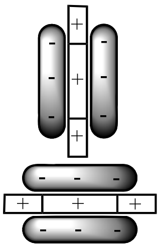
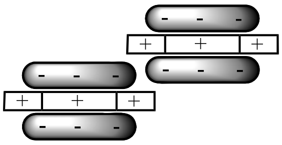


***Figure.** (a) Schematic representation of the herringbone pattern of thiophenol on an Au(111) surface. The grid represents the gold surface and the ellipses the edge view of the benzene ring of the thiophenols. (b) The herringbone packing geometry (gold surface omitted). The large atoms furthest away are the sulfur atoms bond to the surface. (c) Thiophenol. (d) Benzene. (e) Perspective drawing of the herringbone packing geometry.*

   c. Describe the difference between the σ-skeleton and the π-system in benzene in terms of atomic orbital overlap. (2)
      ***Answer:** The overlap between atomic orbitals that results in a σ-bond is, in a first approximation, symmetric with respect to rotation around the bond axis. The size of the overlap is independent on rotation around the bond axis.*
      The π-system is the collection of electrons located in π-orbitals. The overlap of atomic orbitals forming a π-orbital results in a nodal plane passing through the bonded nuclei. Thus these molecular orbitals have the same symmetry as the atomic p-orbitals. The orbital overlap vanishes if one part of the molecule is twisted 90° around the bond axis relative to the other part.

d. Describe the origin of the intermolecular interaction between two benzene molecules and explain why the packing geometry resulting in the herringbone structure is particularly favorable. (4)
Answer: *The π-electrons are located above and below the plane of the molecule leaving behind a slightly electron deficient (positive) σ-system. This interacts with the π-electron cloud of another benzene (π- π interaction). There is two favorable geometries for these interactions.*





The final packing pattern is a result of simultaneous maximization of the intermolecular attractive forces and minimization of the repulsive ones. The former includes the sulfur-gold interaction, the London dispersion forces and the π- π interactions discussed here. The herringbone pattern allows the molecules to close pack in the energetically most favorable way.