Exam
Quantum Engineering (FKA132), Chalmers
2016-12-20

Time and place: 9:00-13:00 on December 20, 2016, Campus Johanneberg.
Examinator: Per Hyldgaard (phone 031 772 8422).
Allowed references: Dictionaries, Beta, Physics Handbook, one handwritten paper of size A4 (both sides) with own notes, and a Chalmers-approved calculator. You can also use the "Extra resources" given at the end of this document.
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. [Six points total]

a) Physical observables are represented by Hermitian operators. Give an example of two physical operators, A and B, for which the commutator is non-zero, $[A, B] \neq 0$.

b) A scanning tunneling microscope can be seen as a one-dimensional barrier problem where electrons move between a tip and a surface reservoir across a region with a high potential value. Using knowledge of steady-state (propagating) wavefunction solutions, give a picture and a brief explanation of the tunneling and state how you expect the current to depend on the tip-surface distance.

c) Consider a quantum-mechanical particle of mass m moving in a three-dimensional potential $V(\mathbf{r})$ that is perfectly isotropic (that is, V depends only on $r = |\mathbf{r}|$; this holds, for example, for an electron in a hydrogen atom). Express the temporal evolution of the particle in terms of the eigenstates and eigenvalues of the time-independent Schödinger equation. Is it possible to pick those eigenstates such that they are also eigenstates of the angular-momentum operator?

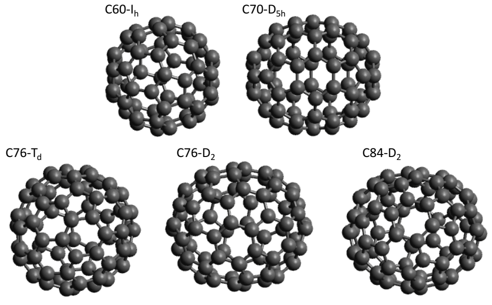

Figure 1: [For question 1.d)] *Computed structure of various carbon Bucky ball molecules.*

d) Bucky balls are pure-carbon molecules with an approximative spherical symmetry, Fig. 1. Consider two examples of such molecules, the C_{60}-I_h and C_{76}-T_d (with 60 and 76 C atoms) which are nearly perfectly round and have a nearly isotropic potential. Assume that each C atom has a mass equal to 12 times the mass of a proton and that both molecules are moving at a kinetic energy equal to room temperature, $k_B T \approx 26$ meV. Compute the de Broglie wavelengths of the C_{60} and C_{76} molecules and discuss differences.

e) Describe briefly why strong hydrogen bonds A–H$\cdots$B are favored by A and B being highly electronegative atoms.

f) Draw a molecular orbital diagram for two interacting atomic orbitals (AOs) that belong to two different atoms. Outline how the covalent bond strength, i.e., the interaction energy, depends on the interaction between two atomic orbitals. What are the two most important parameters?

Problem 2. [6 points total]

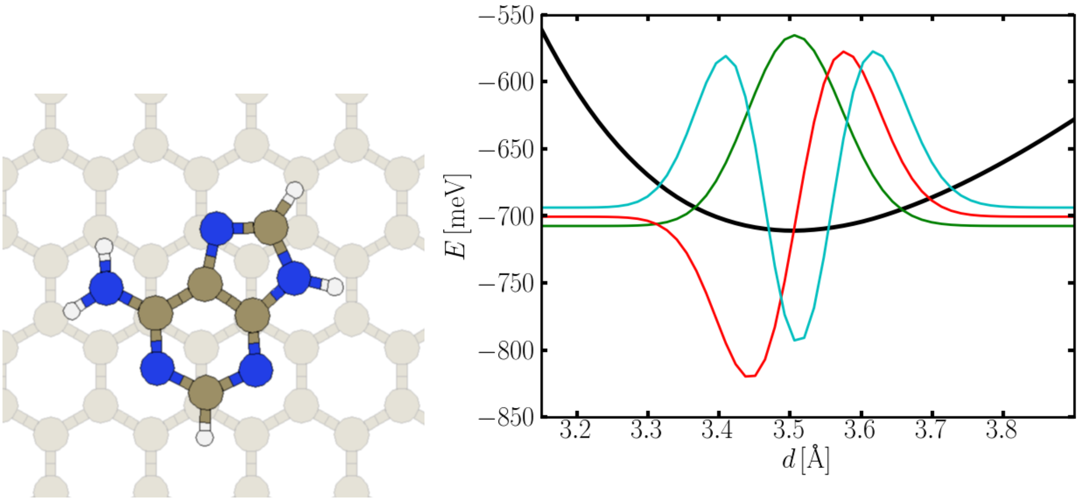

Figure 2: [For problem 2] *Schematics* [left panel] *and computed variation in the weak-chemisorption energy* $E(d)$ [right panel] *of adenine molecules on graphene. The binding-energy variation defines an effective one-dimensional potential* $V(z) = E(z = d)$ *for the quantum-mechanical dynamics (zero-point energy vibrations and excitations) of adenine on graphene. The right panel also shows the wavefunctions for the lowest three eigenvalues of the Hamiltonian defined by* $V(z)$ *and the adenine mass* M*.*

Adenine molecules (a building block for DNA) are relatively strongly bound (≈ 0.7 eV) on graphene in a so-called weak-chemisorption process that partly reflects van der Waals forces; the system has been theoretically characterized by E. Schröder and co-workers [Journal of Physics: Condensed Matters **23**, 135001 (2011)].

The left panel of Fig. 2 shows a schematics of the adsorbtion while the right panel shows the variation (with molecule-surface distance z) in the computed adsorption potential $V(z)$. The right panel of Fig. 2 also shows the wavefunctions $\Phi_{n=0,1,2}$ corresponding to the lowest three eigenvalues $E_{n=0,1,2}$ for the molecule dynamics in this potential $V(z)$.

To lowest order we can approximate the adenine-surface binding by a one-dimensional harmonic oscillator form

$$V_0(z) = \frac{1}{2} M\omega^2 (z - z_{\min})^2 - E_{\min}, \tag{1}$$

where M is the mass of the adenine molecule. The difference from the full-calculation description [given by $V(z)$] is approximated by adding a perturbation term $\hat{H}' = -\frac{1}{3}\lambda\alpha^3 z^3$, with $\alpha = \sqrt{M\omega/\hbar}$. This term describes $V(z) - V_0(z)$ near the minimum at z_{min}.

a) Sketch the first three wavefunctions of the harmonic-oscillator model, given by $V_0(z)$, for the adenine dynamics. Do you expect these to be qualitatively similar to the $V(z)$-wavefunctions (full-problem solutions) $\Phi_{n=0,1,2}$ shown in the right papel of Fig. 2? Discuss! (There is no need to also compare numbers in this question) .

b) Write the perturbation $\hat{H}'$ in terms of the annihilation and creation operators $\hat{a}$ and $\hat{a}^\dagger$, defined by

$$\hat{a} = \frac{\alpha}{\sqrt{2}}(\hat{z} + i\frac{\hat{p}_z}{\hbar\alpha^2}) \tag{2}$$

and its hermitian conjugate $\hat{a}^\dagger$.

c) Using perturbation theory and the properties of the creation and annihilation operators, show that the first-order correction to the energy is zero for all energy levels.

In the last partial question, we also consider the effects of an external radiation, represented by the Hamiltonian

$$H_{\mathrm{rad}}(t) = Az\cos(\omega_{\mathrm{rad}}t), \tag{3}$$

where ω_{rad} can be tuned to optimize any given transition. The rate of radiation-induced excitations out of the ground state can then be treated by comparing the size of the matrix element that enters in Fermi golden-rule estimates:

$$\Gamma_{0\to n} \propto |\langle\Phi_n|z|\Phi_0\rangle|^2. \tag{4}$$

d) Assume that the adenine adsorbates are initially found in the ground state, represented by $|\Phi_0\rangle$. Show that the external radiation [described by $H_{\mathrm{rad}}(t)$], when tuned to the relevant excitation energies, will induce far fewer transitions to state $|\Phi_2\rangle$ than to $|\Phi_1\rangle$. Here it may be useful to the exploit that the wavefunctions have an approximative symmetry or antisymmetry with respect to reflections around the distance z_{min} with minimal-potential energy, Fig. 2.

Problem 3. [6 points total]

A particle of mass m moves in a one-dimensional potential well given by

$$V(x) = \begin{cases} \infty & \text{for } x < -b \\ \eta\left(\frac{\pi x}{2b}\right)^2 & \text{for } -b < x < b \\ \infty & \text{for } b < x \end{cases} \tag{5}$$

where $\eta < 0$ is an energy small compared to the ground-state energy. The potential is illustrated in Fig. 3.

a) Suggest a useful splitting of the problem into an unperturbed starting system $\hat{H}_0$ and a perturbation term $\hat{H}_1$. Argue why it is reasonable to use perturbation theory for finding the eigenstates and eigenenergies of the system.

b) Calculate the eigenenergy for the lowest state of the system given above to first order

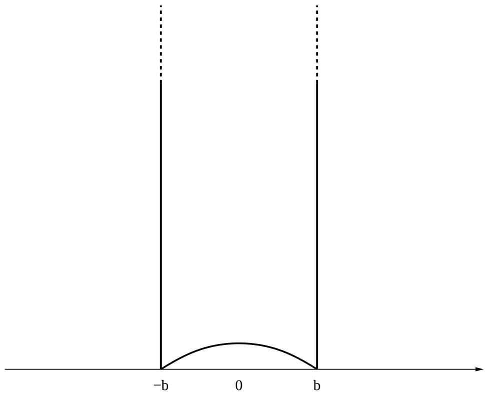

Figure 3: *Sketch of the potential $V(x)$ in problem 3.*

in the perturbation $\hat{H}_1$. It may be useful to use the 'Extra resources" at the end.
c) At approximately which value of η (expressed in a condition that reflects the values of b and m) does it become unreasonable to apply perturbation theory for this problem?

Problem 4. [6 points total]

Consider electrons in a homogeneous magnetic field $\mathbf{B} = B_0(0,1,0)$, where $(0,1,0)$ denotes a vector in the y direction. We focus on the spin Hamitonian

$$\hat{H} = -\frac{1}{\mu_0}\boldsymbol{\mu}\cdot\mathbf{B}\,, \qquad\qquad \boldsymbol{\mu} = -\frac{g\mu_B}{2}\boldsymbol{\sigma} \tag{6}$$

where μ_0 is the magnetic permability, $\mu_B = e\hbar/(2m_e c)$ is Bohr magneton, $g \approx 2.00$, and where $\boldsymbol{\sigma}$ represents the Pauli spin matrices.

a) Calculate the eigenvalues and the (normalized) eigenvectors of the hamiltonian $\hat{H}$, expressed in terms of electon spinors.

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, $P_\downarrow(t)$ (seen relative to direction z), as a function of the time $t > 0$.

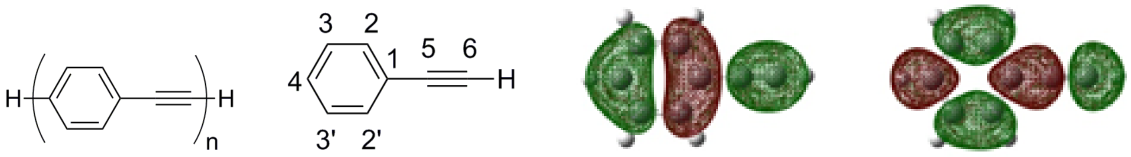

Figure 4: [For Problem 5] *Structure diagrams of Poly(1,4-phenylene-ethynyl) and ethynylbenzene* [first two panels] *and wavefunctions of the HOMO and LUMO levels of the ethynylbenzene monomer* [last two panels].

Problem 5. [6 points total]

Conjugated organic molecules such as poly(1,4-phenyleneethynylene) are investigated as potential candidates to be used as molecular wires in molecular electronics and in nanotechnology. The repeating unit (building block) in the polymer is shown below. So are the highest occupied and lowest unoccupied molecular orbitals for the monomer ethynylbenzene.

a) To which class of molecular orbitals are HOMO and LUMO designated, σ or π, and what is the definition of such an orbital?

b) Give a mathematical expression for the HOMO wave function in terms of suitable atomic orbitals ϕ_i, where i is the atom number shown in the structure of ethynylbenzene above. Numerical values for the constants used in your expression are not needed but the correct signs must be shown. What atomic orbital does ϕ_i correspond to?

c) Will the HOMO-LUMO gap increase or decrease with increasing number of repeating units in the polymer? Rationalize your answer briefly.

d) Draw the orbital shapes for the HOMO and the LUMO of the shortest possible polymer of ethynylbenzene, the dimer shown below.

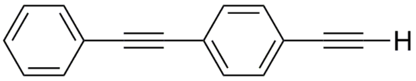

Figure 5: [For question 5.d)] *The shortest possible polymer of ethynylbenzene.*

e) Compounds similar to the dimer shown above are also used as liquid crystals. What are the two most important intermolecular forces between molecules in assemblies of such compounds? Describe briefly the origin of each one of these two forces.

Extra resources

You may find it useful to know the following indefinite-integral results

$$\begin{aligned}
\int \sin^2(y)\,dy &= \frac{y}{2} - \frac{\sin(2y)}{4y} \\
\int \cos^2(y)\,dy &= \frac{y}{2} + \frac{\sin(2y)}{4y} \\
\int y^2 \sin^2(y)\,dy &= \frac{y^3}{6} - \frac{y}{4}\cos(2y) - \frac{1}{4}\left(y^2 - \frac{1}{2}\right)\sin(2y). \\
\int y^2 \cos^2(y)\,dy &= \frac{y^3}{6} + \frac{y}{4}\cos(2y) + \frac{1}{4}\left(y^2 - \frac{1}{2}\right)\sin(2y).
\end{aligned}$$

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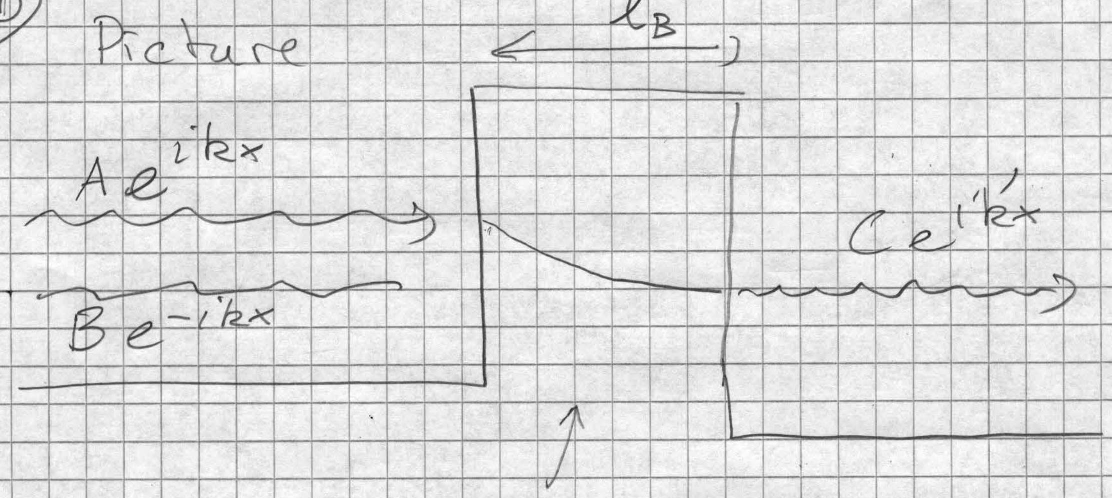
Solutions FKA132 re-sit exam Dec. 2016

1a) Examples $\hat{A} = \hat{x}$ & $\hat{B} = \hat{p}_x$. Then Heisenberg relations says $[\hat{A}, \hat{B}] = [\hat{x}, \hat{p}_x] = i\hbar$.

1b)

Picture



exponential decay of amplitude ratio $|C|/|A|$.

$$\text{Current} \propto \left|\frac{C}{A}\right|^2 = e^{-2\kappa l_B}.$$

If you have a full evaluation of 'T' (for k=k') then that also works.

1c) $$\hat{H} = \frac{\bar{p}^2}{2m} + V(|r|)$$

Eigenstates $\hat{H}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle$

Evolution

$$|\psi(t)\rangle = \sum_i e^{-i\varepsilon_i t/\hbar} c_i |\psi_i\rangle$$

where c_i defines wave function at $t=0$:

$$|\psi(t=0)\rangle = \sum_i c_i |\psi_i\rangle$$

Angular momentum can be used

Also: Yes angular momentum operator $\hat{L}$ commutes with $\hat{H}$ - because of spherical symmetry.

The $\hat{H}$ eigenstates can be chosen to also be eigenvectors for $\hat{L}^2$ and one component, say $\hat{L}_z$ of $\hat{L}$. (as it is often done when we discuss atomic structure and talk of s, p, d, f orbitals, etc.

Note that $[\hat{L}_x, \hat{L}_z] \neq 0$ (etc) so you can only pick one component of $\hat{L}$ for your eigenstates.

1d) For free-particle dynamics $E_{kin} = p^2/2M$. and the de Broglie wavelength follows from

$$\lambda = h/p$$

For C_{60} having $M_1 = 720\, m_p$; $m_p = 1.6726 \cdot 10^{-27}$ kg we have (at $E_{kin} = 26$ meV):

$$p_1 = \sqrt{2M_1 E_k} = 10^{-22}\ \mathrm{kg\,m/s}$$

For C_{76} having $M_2 = 912\, m_p$,

$$P_2 = \sqrt{2M_2 E_k} = \sqrt{\frac{912}{720}}\, p_1$$

$$= 1.12 \cdot 10^{-22}\ \mathrm{kg\,m/s}.$$

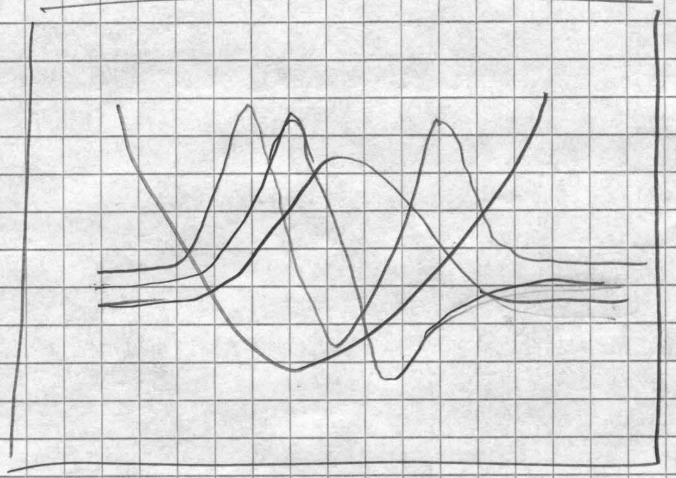
The corresponding wavelengths are

$\lambda_1 = 6.6$ pm and $\lambda_2 = 5.9$ pm.

The wavelength is small for heavy molecules... and for (macroscopic objects!)

1e) + 1f) Please see separate document for solutions to the chemistry questions.

2a) First three wavefunction of Hamomic oscillator potential



These are almost exactly the same as those found for the computed potential V(z) and shown in Fig 2 of the problem set. This is because the approximation V_0 is ok near the bottom of the adsorption well and because when considering perturbations the effects are found primarily in the energies and not in wave functions. We may, for instance, compute the first-order energy shifts from unperturbed wave functions (and second-order shifts in energis from first order corrections in wavefunctions).

2b) $\hat{a} = \frac{\alpha}{\sqrt{2}}\left(\hat{z} + i\frac{\hat{p}}{\hbar\alpha^2}\right)$; $\hat{a}^+ = \frac{\alpha}{\sqrt{2}}\left(\hat{z} - i\frac{\hat{p}}{\hbar\alpha^2}\right)$.

$\hat{z} = \frac{1}{\sqrt{2}\alpha}(\hat{a} + \hat{a}^+)$. Thus $\hat{H}' = -\frac{1}{3}\frac{\lambda}{2^{3/2}}(\hat{a} + \hat{a}^+)^3$.

2c) First order shift of any level?

Note. $(a+a^{+})^3 = \hat{a}\hat{a}\hat{a} + \hat{a}^{+}\hat{a}^{+}\hat{a}^{+} + a$

$$\hat{a}\underbrace{(\hat{a}\hat{a}^{+}+\hat{a}^{+}\hat{a})}_{=1} + a^{+}\underbrace{(\hat{a}\hat{a}^{+}+\hat{a}^{+}\hat{a})}_{=1}$$

$$= \hat{a}\hat{a}\hat{a} + \hat{a}^{+}\hat{a}^{+}\hat{a}^{+} + \hat{a} + \hat{a}^{+}.$$

But for any harmonic-oscillator state $|n\rangle$ we have

$$\hat{a}|n\rangle \propto |n-1\rangle \quad \& \quad \hat{a}^{+}|n\rangle \propto |n+1\rangle$$

and hence

$$\langle n|\hat{a}|n\rangle = \langle n|\hat{a}^{+}|n\rangle = 0.$$

Similarly + $\langle n|\hat{a}^3|n\rangle = \langle n|\hat{a}^{+}|n\rangle = 0$

and

$$\delta\varepsilon_i^{(1)} = \langle n|\hat{H}'|n\rangle = 0 \text{ for all } n.$$

2d) We need to compare

$\langle\phi_2|z|\phi_1\rangle$ and $\langle\phi_1|z|\phi_1\rangle$

In the harmonic-oscillator approximation the $[\hat{a},\hat{a}^{+}]$ argument [in 2c)] would tell us that the first is explicitly zero and the second is not – but now we work with the $V(z)$ wave functions $|\phi_n\rangle$.

Yet parity - evident in the right-hand-side panel of fig 2 - comes to rescue.

Making the coordinate transformation $z \to z' = -z$ we have

$$\langle\phi_2|z|\phi_0\rangle = \int_{-\infty}^{\infty} dz\ \phi_2^*(z)\, z\, \phi_0(z)\, dz$$

$$\simeq -\int_{-\infty}^{\infty} dz'\ \phi_2(z')\, z'\, \phi_0(z')\, dz'$$

And thus $\langle\phi_2|z|\phi_0\rangle \simeq 0$.

· Meanwhile,

$$\langle\phi_1|z|\phi_0\rangle = \int_{-\infty}^{\infty} \phi_1(z)\, z\, \phi_0(z)\, dz$$

$$\simeq \int_{-\infty}^{\infty} \phi_1(z')\, z'\, \phi_0(z')\, dz'$$

and there is no argument that $\langle\phi_1|z|\phi_0\rangle$ should be small - which it is not.

Note If you have chosen to solve this argument based on step-operators and the point that the wavefunctions can not differ from those of the Harmonic oscillator case then that is also accepted.

⑥

A particle of mass m in

$$V(x) = \begin{cases} \infty \\ \eta\left(\frac{\pi x}{2b}\right)^2 & \text{for } -b<x<b \\ \infty \end{cases}$$

$$\hat{H}_0 = \frac{p^2}{2m} + V_0(x) \quad \text{where}$$

$$V_0(x) = \begin{cases} \infty \\ 0 & \text{for } -b<x<b \\ \infty \end{cases}$$

squarewell potential.

Perturbation $\hat{H}_1 = \eta\left(\frac{\pi x}{2b}\right)^2$.

Note: variations on this theme is possible.

Perturbation theory? As long as $\eta \to 0$ then H_0 is a good starting point since we allready know the eigen states

$$E_{n=1,2,\dots} = \frac{\hbar^2 \pi^2 n^2}{2m(2b)^2}$$

$$\psi_{n=1}(x) = \sqrt{\frac{1}{N_1}} \cos\left(\frac{\pi x}{2b}\right)$$

$$\psi_{n=2}(x) = \sqrt{\frac{1}{N_2}} \sin\left(\frac{\pi x}{2b}\right)$$

Value of N_1? Use extra materials to find $N_1 = b$.

3b) Firstorder perturbation theory

$$\delta E^{(1)}_{n=1} = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle$$

$$= \eta \int_{-b}^{b} \left(\frac{1}{b}\right) \cos^2\left(\frac{\pi x}{2b}\right) \cdot \left(\frac{\pi x}{2b}\right)^2 dx \quad \left\{ \begin{array}{l} y = \frac{\pi x}{2b} \\ dy = \frac{\pi}{2b} dx \end{array} \right.$$

$$= \eta \left(\frac{2\cancel{b}}{\pi \cancel{b}}\right) \int_{-\pi/2}^{\pi/2} y^2 \cos^2 y \, dy$$

$$= \eta \left(\frac{2}{\pi}\right) \left[\frac{\overbrace{y^3}^{\text{odd}}}{6} + \overbrace{\frac{y}{4} \cos(2y)}^{\text{odd}} + \overbrace{\frac{1}{4} \left(y^2 - \frac{1}{2}\right) \sin(2y)}^{[= 0 \text{ at } \pm \pi/2]} \right]_{-\pi/2}^{\pi/2}$$

$$= \eta \left(\frac{2}{\pi}\right) \left[\frac{2}{6} \left(\frac{\pi}{2}\right)^3 - \frac{\pi}{4} \right] = \eta \underbrace{\left[\frac{1}{3} \left(\frac{\pi}{2}\right)^2 - \frac{1}{2} \right]}_{\simeq 1/3}$$

Note that shift can appear differently with another $\hat{H}_1$ definition. <u>But</u>: $E_{n=1} + \delta E^{(1)}_{n=1}$ same.

3c) Breakdown? Ex. compare zeropoint energy [that is value of $E_{n=1}$] with $\delta E^{(1)}_{n=1}$. We desire

$$\eta \left[\frac{1}{3} \left(\frac{\pi}{2}\right)^2 - \frac{1}{2} \right] << \frac{\hbar^2 \pi^2}{8 m b^2}$$

Or

$$\eta << \frac{\hbar^2}{2mb^2} \left[\frac{3}{\pi^2 - 6} \right] \approx \frac{3}{4} \frac{\hbar^2}{2mb^2}$$

Note that criteria can look different if you had used a different splitting into $\hat{H}_0$ and $\hat{H}_1$ or formulated it differently. But principle is the same.

Problem 4

$$\overset{\alpha>0}{H = \alpha\,\sigma_y}\ ;\ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

4a) Eigenvalues/Eigenstates ?

$\chi_\pm = \begin{pmatrix} \alpha_\pm \\ \beta_\pm \end{pmatrix}$ satisfying

$$\sigma_y \begin{pmatrix} \alpha_\pm \\ \beta_\pm \end{pmatrix} = \pm \begin{pmatrix} \alpha_\pm \\ \beta_\pm \end{pmatrix} \quad \left\{ \begin{array}{l} '+' \longleftrightarrow \uparrow \\ '-1' \Longleftrightarrow \downarrow \end{array} \right.$$ in $\hat{y}$ direction.

$\chi_{y\uparrow} \equiv \chi_{'+'} \equiv \begin{pmatrix} \alpha_+ \\ \alpha_\beta \end{pmatrix}$ we see solution $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$.

Also $\chi_{y\downarrow} = \chi_{'-'} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$.

Orthonormality checks: $\chi_{\uparrow y}^\dagger \cdot \chi_{\downarrow y}$

$$\chi_{\uparrow y}^\dagger \cdot \chi_{\downarrow y} = \frac{1}{2}(1, -i)\begin{pmatrix} 1 \\ -i \end{pmatrix} = \frac{1}{2}[1-1] = 0 \text{ . ok.}$$

$$\chi_{\uparrow y}^\dagger \cdot \chi_{\uparrow y} = \frac{1}{2}(1, -i)\begin{pmatrix} 1 \\ i \end{pmatrix} = 1, \text{ etc.}$$

Eigenenergies

highest $\quad \hat{H}\,\chi_{\uparrow y} = +\overbrace{\frac{g N_B}{2 N_0}}^{\alpha} B_0\, \chi_{\uparrow y} \simeq B_0 \frac{N_B}{N_0}\, \chi_{\uparrow y} \equiv \underline{\underline{\overset{\varepsilon_2 \equiv \hbar\omega_B > 0}{\varepsilon_2}\, \chi_{\uparrow y}}}$

lowest $\quad \hat{H}\,\chi_{\downarrow y} = -B_0 \frac{N_B}{N_0}\, \chi_{\downarrow y} \equiv \varepsilon_1\, \chi_{\downarrow y}\ ;\ \varepsilon_1 = -\varepsilon_2 < 0$

4b) Problem at $t=0$; $\chi(t=0) \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

But $\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \gamma_0\, \chi_{\uparrow y} + \delta_0\, \chi_{\downarrow y} = \begin{pmatrix} \gamma_0 + \delta_0 \\ (\gamma_0 - \delta_0)\, i \end{pmatrix}$

for $\gamma_0 = \delta_0 = \frac{1}{\sqrt{2}}$.

Thus probability for measing $\uparrow y'$ is

$P_{\uparrow y'} = 1/2$. Similarly $P_{\downarrow y} = 1/2$ at $t=0$.

4c) Time evolution ?

Formally $\chi(t) = \sum_n c_n e^{-i\varepsilon_n t/\hbar} \chi_n$ by Schrödinger Equation

Since $\varepsilon_2 \equiv \hbar\omega_B \simeq B_0 \frac{N_B}{N_0}$ and $\varepsilon_1 = -\hbar\omega_B \simeq -B_0 \frac{N_B}{N_0}$
we have

$$\chi(t) = \frac{1}{\sqrt{2}} e^{-i\varepsilon_2 t/\hbar} \chi_{\uparrow y} + \frac{1}{\sqrt{2}} e^{-i\varepsilon_1 t/\hbar} \chi_{\downarrow y}$$

$$= \frac{1}{2}\begin{pmatrix} \{e^{-i\omega_B t} + e^{+i\omega_B t}\} \\ i\{e^{-i\omega_B t} - e^{+i\omega_B t}\} \end{pmatrix}$$

$$= \begin{pmatrix} \cos\omega_B t \\ -\sin\omega_B t \end{pmatrix} = \cos(\omega_B t)\,\chi_{\uparrow z} - \sin(\omega_B t)\,\chi_{\downarrow z}.$$

4d) $P_{\uparrow z}(t)$ is $|\langle\chi_{\uparrow z}|\chi(t)\rangle|^2$ (etc).

so $P_{\uparrow z} = P_\uparrow = \cos^2(\omega_B t)$

$P_{\downarrow z} = P_\downarrow = \sin^2(\omega_B t)$

Sanity check

$$P_{\downarrow z} + P_{\uparrow z} = \cos^2(\omega_B t) + \sin^2(\omega_B t) = 1$$

For problem 5 please see separate solution note for chemistry problems/questions.

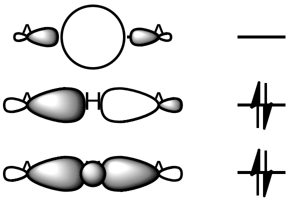
Answers to chemistry problems/questions at FKA132 re-exam, December 2016.

Problem 1) [Chemistry part]

1e) Describe briefly why strong hydrogen bonds A–H·····B are favored by A and B being highly electronegative atoms.

Answer:

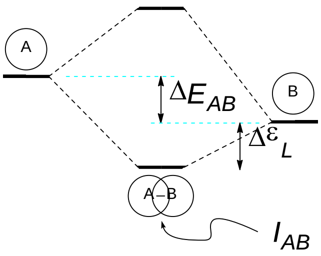
The hydrogen bond is in the covalent limit a four-electron three-center bond:



The four electrons will mainly be localized to the two atoms A and B. This is favored if these atoms are highly electronegative.

1f) Draw a molecular orbital diagram for two interacting atomic orbitals (AOs) that belong to two different atoms. Outline how the covalent bond strength, i.e. the interaction energy, depends on the interaction between two atomic orbitals. What are the two most important parameters?

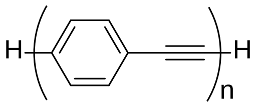
Answer:



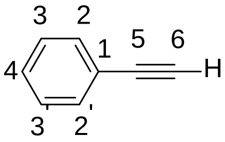
The two most important parameters are the orbital overlap integral ***I_{AB}*** *and the difference in energy* ***ΔE_{AB}*** *for the two interacting orbitals. The larger the orbital overlap integral is and the smaller the energy difference is the larger the interaction energy will be, and thus the stronger the covalent bond will be.*

Problem 5) [Chemistry]

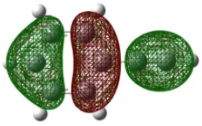
Conjugated organic molecules such as poly(1,4-phenyleneethynylene) are investigated as potential candidates to be used as molecular wires in molecular electronics and in nanotechnology. The repeating unit (building block) in the polymer is shown below. So are the highest occupied and lowest unoccupied molecular orbitals for the monomer ethynylbenzene.



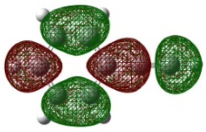
Poly(1,4-phenylene-ethynyl)



ethynylbenzene



HOMO



LUMO

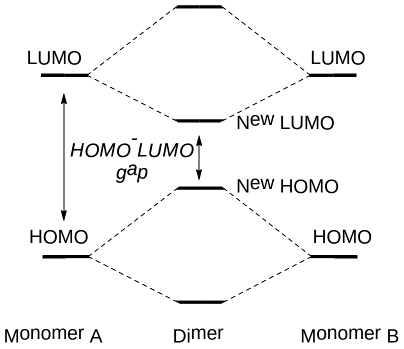
a. To which class of molecular orbitals are HOMO and LUMO designated, σ or π, and what is the definition of such an orbital?
Answer:
Both HOMO and LUMO are π-orbitals. A π-orbital has a nodal plane that coincides with the bond axis.

b. Give a mathematical expression for the HOMO wave function in terms of suitable atomic orbitals φ_i, where *i* is the atom number shown in the structure of ethynylbenzene above. Numerical values for the constants used in your expression are not needed but the correct signs must be shown. What atomic orbital does φ_i correspond to?
Answer:
The atomic orbitals φ_i to which the molecular orbital HOMO can be traced back to are the carbon-$2p_z$ orbitals.

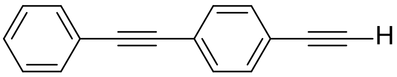
$$\psi_{HOMO} = C_4 2p_z(4) + C_{3,3'}[2p_z(3) + 2p_z(3')] - C_{2,2'}[2p_z(2) + 2p_z(2')] - C_1 2p_z(1) + C_5 2p_z(5) + C_6 2p_z(6)$$

Where all coefficients $C_i > 0$.

c. Will the HOMO-LUMO gap increase or decrease with increasing number of repeating units in the polymer? Rationalize your answer briefly.
Answer:
The HOMO-LUMO gap will decrease, see the interaction diagram for two units (monomers) forming one dimer.



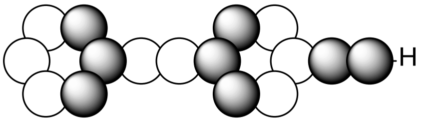
d. Draw the orbital shapes for the HOMO and the LUMO of the shortest possible polymer of ethynylbenzene, the dimer shown below.



Answer:

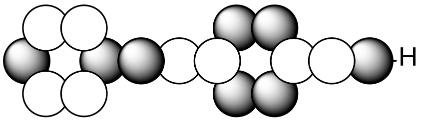
The new HOMO(dimer) is constructed by linear combination of one HOMO orbital from each monomer in an antibonding fashion:

$$New\ HOMO = HOMO(Monomer\ A) - HOMO(Monomer\ B).$$

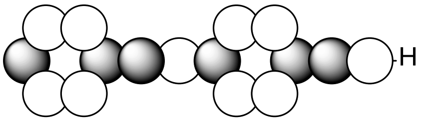


The new LUMO(dimer) is constructed by linear combination of one LUMO orbital from each monomer in a bonding fashion:

$$New\ LUMO = LUMO(Monomer\ A) - LUMO(Monomer\ B).$$



The other combination gives an additional node and is higher in energy (LUMO+1):



e. Compounds similar to the dimer shown above are also used as liquid crystals. What are the two most important intermolecular forces between molecules in assemblies of such compounds. Describe briefly the origin of each one of these two forces.

Answer:

The two most important intermolecular forces between molecules similar to the dimer shown above are π-interactions and van der Waals interactions.

The origin of the π-interactions is the interaction between the "electron deficient" σ-skelton and the "π-electron cloud".

van der Waals interactions can be divided into dispersion (London) interactions and exchange (Pauli)–repulsion. The London dispersion force is a weak intermolecular force arising from quantum induced instantaneous polarization multipoles in molecules.