Exam
Quantum Engineering (FKA132), Chalmers
2016-10-26

Time and place: 14:00-18:00 on October 26, 2016, Campus Johanneberg.
Examinator: Per Hyldgaard (phone 031 772 8422; mobile phone 076 1010 581).
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. [Six points total]

a) State the main idea, key result, and usefulness of Bohr's atom model.

b) Explain the relevance of a superposition principle in a wave description of the electron behavior. You can, for example, list and discuss phenomena or experiments where superposition is needed for a theoretical account.

c) Calculate the de Broglie wavelength of neutrons and electrons at kinetic energies corresponding to 4K and to room temperature. Explain why thermal neutrons are an ideal tool for a mapping of the atomic structure of crystaline material; It may be useful to recall that the scattering of waves enhances dramatically when the wavelength matches the length scale of the potential variation.

d) Discuss the difference between the regular, i.e., time-dependent, and the time-independent Schrödinger equations. Also, define the energy expectation value and describe the variational approach to estimating the ground-state energy E_0 of a system. Show that this estimate will be an *upper* bound on the value of E_0.

e) What defines a bonding molecular orbital?

f) One basic assumption in Hückel theory is that the atomic orbitals (p_z) contributing to the π-bonding in a planar molecule can be treated independently from the atomic orbitals contributing to the σ-bonding in the molecule. Why is this assumption valid?

Problem 2. [6 points total]

The combination of van der Waals (vdW) attraction and Pauli exclusion interactions between two noble-gas atoms or small molecules separated by distance R can sometimes be modeled by the so-called Lennard-Jones potential

$$V(R) = \epsilon \left\{ \left(\frac{R_m}{R} \right)^{12} - 2 \left(\frac{R_m}{R} \right)^{6} \right\} . \tag{1}$$

Here $-\epsilon$ is the potential minimum and R_m is the position of the minimum. You can

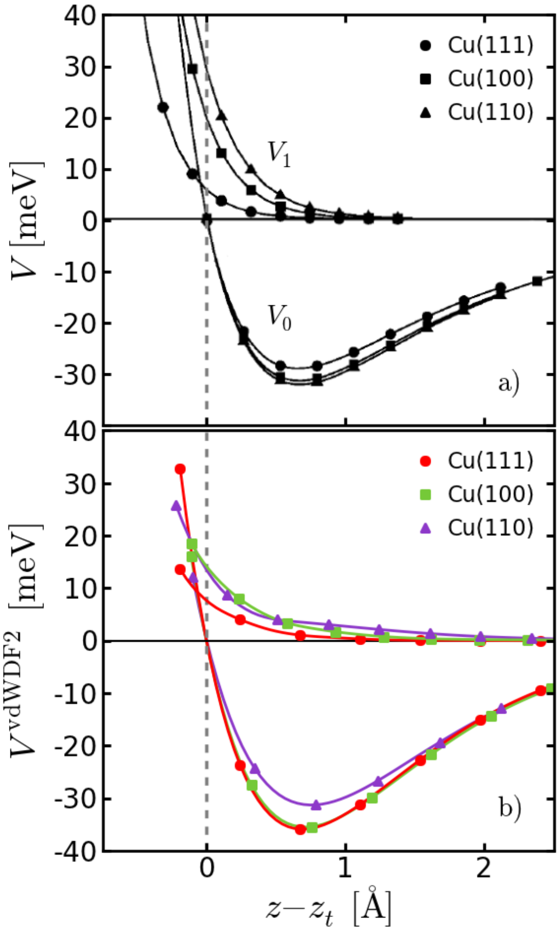

Figure 1: Binding-energy curves for H_2 physisorption on various types of Cu surfaces (left panel) The top panel shows date reconstructed from experimental observation where as the bottom panel shows results of a recent vdW-DF calculation.

assume that R_m and ϵ have been fitted by either measurements or accurate calculations of the interatomic forces.

a) Extract an effective model of the vibrational dynamics. In other words, find the best-fit parameters for an harmonic-oscillator model Hamiltonian

$$H_{\text{vib}} = \frac{P_{\tilde{R}}^2}{2m} + \frac{1}{2} m \omega_{\text{vib}}^2 \tilde{R}^2 - \epsilon \,. \tag{2}$$

Express the model parameter ω_{vib} in terms of the reduced mass m and of R_m and ϵ. Explain why you need the offset and why $m = M/2$ for a system comprising two identical molecules of mass M. [2 points]

b) Discuss the accuracy of the vibrational modeling. First determine the excitation energies of the harmonic-oscillator model. Then answer the question: How do you expect these vibrational frequencies to relate to those of the more relevant Lennard-Jones model potential? As a part of the discussion, sketch and compare the variation in the Lennard-Jones and in the model potential of Eq. (2). [2 points]

Fig. 1 shows the variation of the effective potential $V(z)$ for H_2 molecules physisorbed on various Cu facets (various types of Cu surfaces). The curves are extracted from Chalmers experiments (top panel) and from a DFT study using the Chalmers-Rutgers vdW-DF method (bottom panel). The Pauli exclusion principle gives rise to repulsion (set of curves marked 'V_1') that are dramatic at short molecule-to-surface separations z. However, the electron-density overlap – and therefore repulsion – also decays exponentially with increasing separation and the vdW attraction therefore provides a net attraction outside the so-called classical turning point, marked as z_t. The potentials $V(z)$ extracted from experiment and from vdW-DF calculations are unchanged for physisorption of deuterium molecules D_2.

c) Use knowledge of the hydrogen-molecule mass and vdW-DF calculations for the Cu(111) surface to predict the vibrational levels (given in meV) for the physisorption well? How large is the molecular zero-point energy value? How do your predictions change for D_2? [2 points]

Problem 3. [6 points total]

Consider a model of an atom in which the electron dynamics is assumed fully characterized as a one-dimensional harmonic-oscillator problem

$$\hat{H}_a = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega_{\text{eff}}^2 \hat{x}^2 - \epsilon_{\text{eff}} \,, \tag{3}$$

given by an effective oscillator frequency ω_{eff}. The offset $-\epsilon_{\text{eff}}$ ensures that the electrons are bound, i.e., that the lowest-lying state(s) have an energy smaller than the spectrum of free-electron states, at $E_k^{\text{free}} = (\hbar k)^2/(2m)$.

The model Eq. 3 can also be characterized by creation $\hat{b}^+$ and annihilation operators $\hat{b}$, given by

$$\hat{b} = \frac{m\omega_{\text{eff}}\hat{x} + i\hat{p}_x}{\sqrt{2\hbar m \omega_{\text{eff}}}} \,. \tag{4}$$

a) Sketch the form of the first two oscillator eigenfunctions, $\psi_0(x)$ and $\psi_1(x)$, showing also the potential. Furthermore, express $\hat{H}_a$ in terms of $\hat{b}$ and $\hat{b}^+$. [1 point]

b) The atom is subjected to an external radiation field $E(t) = E_{\text{ext}} \cos(\omega t)$, giving rise to a perturbation $H_1(t) = -eE_{\text{ext}} \cos(\omega t)\, \hat{x}$. Express $H_1(t)$ in terms of $\hat{b}$ and $\hat{b}^+$. [1 point]

c) Compute the first-order and second-order energy shifts for the lowest-energy state in the limit of steady-state (or $\omega \ll \omega_{\text{eff}}$). [1 point]

d) Assume that the system begins in the ground state $n = 0$ when we initate the external radiation. Compute the rate of transition to the first excited ($n = 1$) state as a function of the angular frequency ω of the radiation. [1 point]

Consider next two such model atoms, characterized by the same ω_{eff} at large enough separations R that you can also ignore both chemical interactions and Pauli exclusion. The atoms have no static dipole or multipole moments. Thus you can also ignore all electrostatic interactions between the atoms. It is tempting to think that the two-atom model Hamiltonian could therefore be described

$$H^0_{2a} = H_{a1} + H_{a2} = \sum_{i=1,2} \frac{\hat{p}^2_{x_i}}{2m} + \frac{1}{2} m \omega^2_{\mathrm{eff}} (\hat{x}^2_1 + \hat{x}^2_2) \tag{5}$$

where x_1 and x_2 denote coordinates of atom '1' and '2', respectively. However, the ground state solution of the atom model, Eq. (3) still reflects a zero-point vibration in the density of charged particles. Such fluctuations cause an inter-atomic coupling mediated by the electrodynamic field. We model this coupling by adding the Hamiltonian term

$$H'_R = -f_R x_1 x_2; \qquad f_R = \frac{e^2/2\pi}{R^3} \,. \tag{6}$$

Below we seek a nonperturbative account of the dispersive or van der Waals (vdW) binding $\Delta E_{\mathrm{vdW}} < 0$ that results from including H'_R in the total two-atom model Hamiltonian $H_{2a}(R) = H^0_{2a} + H'_R$.

e) Show that you can rewrite $H_{2a}(R)$ as a sum of two new, independent harmonic-oscillator terms

$$H_{2a} = \frac{\hat{p}^2_X}{2m} + \frac{\hat{p}^2_Y}{2m} + \frac{1}{2} m \left(\omega^2_{\mathrm{eff}} - f_R/m\right) \hat{X}^2 + \frac{1}{2} m \left(\omega^2_{\mathrm{eff}} + f_R/m\right) \hat{Y}^2 \,, \tag{7}$$

by introducing so-called normal coordinates $\hat{X} = (x_1 + x_2)/\sqrt{2}$ and $\hat{Y} = (x_1 - x_2)/\sqrt{2}$. When establishing the form of, for example, $\hat{p}_X$ it is correct to assume independence of $\hat{x_1}$ and $\hat{x}_2$ so that $[\hat{p}_{x_1}, \hat{x}_2] = 0$, etc. [1 point]

f) Compute the vdW binding energy ΔE_{vdW} by contrasting the ground state expectation value of $\hat{H}_{2a}$ and $\hat{H}^0_{2a}$. [1 point]

Problem 4. [6 points total]

This problem concerns a two-level model system given by eigenenergies $\epsilon_1 \geq \epsilon_0$ and eigenstates $|0\rangle$ and $|1\rangle$. You can assume that $|0\rangle$ and $|1\rangle$ are normalized and orthogonal.

a) Assume that $|0\rangle$ and $|1\rangle$ represent states with different spatial wavefunctions and that you have a number of $s = 1/2$ particles to distribute into these levels. What is the lowest energy configuration of the total system that you can have if you have: 1 particle? 2 particles of opposite spins? 2 particles of same spin? 3 particles? [1 point]

From now on ignore the level degeneracy discussed in 'a)'. Assume that at time $t = 0$ the system is prepared in the normalized quantum state

$$|\psi(t=0)\rangle = \alpha_0 |0\rangle + \beta_0 |1\rangle \,. \tag{8}$$

At a later time t we express the quantum state

$$|\psi(t)\rangle = \exp(i\theta(t)) \{\alpha_0 |0\rangle + c(t) |1\rangle\} \,. \tag{9}$$

b) Identify $\theta(t)$ and show that $c(t) = \beta_0 \exp(-i\omega_{\mathrm{osc}} t)$ where $\omega_{\mathrm{osc}} = (\epsilon_1 - \epsilon_0)/\hbar$ represents a characteristic, so-called Rabi, oscillation of the system. Also compute the probablity of finding eigenenergies ϵ_1 and ϵ_0 as a function of time t. [1 point].

In the remainder of the problem we explore manifestations of the Rabi oscillations.

Assume first that the two-level model describes a wavefunction problem. Also assume that the wavefunctions $\langle x|0\rangle$ and $\langle x|1\rangle$ can be approximated as the first and second eigenstates of the infinite-wall particle-in-a-box potential

$$V_{\text{eff}}(x) = \begin{cases} 0 & \text{if } |x| < d/2\,, \\ \infty & \text{if } |x| > d/2\,. \end{cases} \tag{10}$$

c) Compute the time-dependence in the expectation value of the particle position $\langle x\rangle(t)$ (subject to the assumption that $\alpha_0 = \beta_0 = 1/\sqrt{2}$) and discuss the nature of the Rabi oscillations in this case. [2 points]

Consider next a pure spin system. Consider the dynamics of a beam of Ag atoms moving in a uniform magnetic field directed in spatial direction z but which is also prepared and tested by a pair of Stern-Gerlach (SG) probes. We treat the displacement of the Ag atoms as classical and $H_0 = (\hbar\omega_{\text{osc}}/2)\,\sigma_z + (\epsilon_1 + \epsilon_0)/2$ (where σ_z denotes the Pauli matrix σ_z) describes the quantum spin dynamics. Here, the higher-energy state $|1\rangle$ (lower-energy state $|0\rangle$) corresponds to a spin-up (spin-down) configuration with respect to direction z. The oscillation frequency ω_{osc} is proportional to the magnitude of the homogeneous field.

Inside a SG probe, in which the atoms only spend a vanishing time, the inhomogeneous magnetic field causes the beam of Ag atoms to be split into two. The sorting can be seen as a measurement of the spin polarization according to the direction $\hat{n}$ of the SG inhomogeneous field. The SG beam sorting at a time t is therefore given from knowledge of the Ag state $|\psi(t)\rangle$ and the "spin-up" and "spin-down" eigenstates of the operator that emerges from the dot-product of $\hat{n}$ and the vector of Pauli matrices σ.

d) Show that the initial quantum state Eq. (8), for $\alpha_0 = \beta_0 = 1/\sqrt{2}$, can be seen as arising from performing a SG probe at $t = 0$ with the inhomogeneous field in direction x. Suggest a practical way to engineer any deriable initial state $|\psi(t = 0)\rangle$. [1 point]

e) Assume that beam of Ag atoms enters a second SG with an inhomogenous field in direction x at a later time t, having moved only in the homogenous magentic field in between. Compute the probability (as a function of t) that a given Ag atom will be sorted into either of the second-SG beams. Discuss the nature of the Rabi oscillations in this spin case. [1 point]

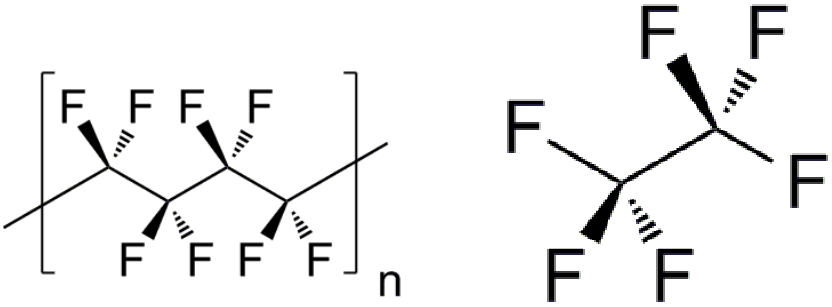

Figure 2: Atom configuration of Teflon (left panel) and Hexafluoroethane (right panel).

Problem 5. [6 points total]

The polymer polytetrafluoroethylene (PTFE/Teflon) is a solid and is often used when a very nonrective (stable) and non-sticky surfaces is needed. The desirable properties of this material is due to the nature of the carbon-fluorine bond and its constitutional elements.

a) Draw an orbital interaction diagram showing the bonding and antibonding molecular orbitals (MOs) corresponding to a carbon-fluorine bond in teflon (left panel of Fig. 2). Use a sp^3-orbital on the carbon atom and a p-orbital on the fluorine atom as the base (starting-point). [1 point]

b) The carbon-fluorine is one of the strongest, if not the strongest, bond in organic chemistry. It is also one of the most polar covalent bonds. Use your orbital interaction diagram to show why the carbon-fluorine is a highly polarized bond. [1 point]

c) Hexafluoroethane (right panel of fig. 2) may be considered as a small model of Teflon. Does this molecule have a large or small dipole moment? [1 point]

d) Explain why Teflon is a non-sticky material. It is both hydrophobic and lipophobic, i.e., it does not shows substantial intermolecular interactions with neither polar compounds nor with non-polar compounds such as hydrocarbons ($C_xH_{(2x+2)}$). [3 points]

FKA132 / Quantum engineering
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Problem I

a) Bohr's atom model

- electron dynamics for hydrogen atom must be in quantized orbitals — or rather in orbits with quantized angular momentum

- $E_n = \frac{Ry}{n^2}$; $n = 1, 2, 3 \ldots$

- $\hbar\omega_{nm} = E_n - E_m$ discrete levels, explains observations including Balmer series of lines.

b) Superposition of waves $\Psi(r,t) = \alpha \cdot \Psi_A + \beta \Psi_B$ Can describe interference as is relevant for Young's double-split experiment, Bragg reflection in crystaline matter, i.e., Davisson-Germer experiment. There are more examples.

c) de Broglie wavelength

$$\lambda = \frac{h}{p}$$, h from e.g. Handbook

Any given temperature T corresponds to a kinetic (particle) energy $E_{kin} = \frac{p^2}{2m} = k_B T$. In turn $p = \sqrt{2m E_{kin}}$ and so you need the electron and neutron mass ($\approx$ proton mass) from the handbook.

electron: $\lambda_e = 2\pi \cdot (\hbar^2/2m_e a_0)^{1/2}/(k_B T)^{1/2} \cdot a_0$

The numerical values for λ_{part} are

T	Neutrons	electrons
4K	$\lambda \simeq 15$ Å	$\lambda \simeq 660$ Å
300K	$\lambda \simeq 2$ Å	$\lambda \simeq 75$ Å

- Thermal neutrons thus have a wavelength ~ 2Å that can easily scatter off the potential defined by the periodic arrangement of atoms in matter.

d) - Regular Schrödinger Equation (SE) describes the time-evolution of quantum states

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H|\psi(t)\rangle$$

- The time-independent SE is a tool we use to find a (complete) set of eigenvalues

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \quad (\text{where } 1 = \sum_n |\psi_n\rangle\langle\psi_n|)$$

From this knowledge we have an easy solution also to the regular SE:

$$|\psi(t)\rangle = \sum_n e^{-iE_n t/\hbar} c_n |\psi_n\rangle .$$

- Energy expectation value?

$$E = \langle \Psi(t) | \hat{H} | \Psi(t) \rangle.$$

(Let $\{|\Psi_n\rangle\}$ be the complete set of eigenvalues,

$$E = \sum_n |\langle \Psi(t) | \Psi_n \rangle|^2 E_n$$

where $|\langle \Psi(t) | \Psi_n \rangle|^2$ is the probability for observing eigenenergy E_n)

- Variational approach to finding groundstate E_0

For any guess for a normalized wave-function Ψ then

$$E_\Psi \equiv \langle \Psi | \hat{H} | \Psi \rangle = \sum_n |\langle \Psi | \Psi_n \rangle|^2 E_n$$

$$\geq \sum_n |\langle \Psi | \Psi_n \rangle|^2 E_0 = E_0$$

<u>So</u>: make a good guess Ψ, a function that can depend on a set of parameters $\{\alpha, \beta, \gamma, \ldots \Omega\}$. Next vary $\{\alpha, \beta, \ldots\}$ to minimize E_Ψ. It is an upper bound because $E_\Psi \geq E_0$ for <u>all</u> wavefunctions

e) see separate sheet of chemistry answers

f) see separate sheet of chemistry answers

Problem II

a) Best-fit parameters for Lennard-Jones potential (V(R) for van der Waals attraction pauli repulsion) among two molecules.

- First note that the vibrations are naturally described in coordinate system with separation R. and a reduced mass

$$m = \frac{M_1 M_2}{M_1 + M_2} \longrightarrow \frac{M}{2} \text{ for } M_1 = M_2 = M.$$

- We have the potential V(R) in this coordinate system and we simply expand to second order around R_m:

$$V(R) \simeq V(R_m) + \frac{1}{2} \left.\frac{\partial^2 V}{\partial R^2}\right|_{R_m} (R - R_m)^2$$

Compare harmonic oscillator moder

$$V(\tilde{R} = R - R_m) = \underbrace{V(R_m)}_{\substack{\text{negative offset} \\ = -\varepsilon}} + \frac{1}{2} k \tilde{R}^2 .$$

So $k = m\omega_{vib}^2 = \frac{\partial^2 V}{\partial R^2} = 72 \frac{\varepsilon}{R_m^2}$

$$\omega_{vib} = \frac{6\sqrt{2}}{R_m} \sqrt{\frac{\varepsilon}{m}} .$$

- Excitation given by $\hbar\omega_{vib}$, $E_0 = \frac{1}{2}\hbar\omega_{vib}$

b) - Accuracy?
(In scaled coordinates $x = R/R_m$)

$$V(R) = \varepsilon\, x^{-12}\{1 - 2x^6\}$$

$$V_{ham}(R) = 36\,\varepsilon\, \underbrace{\{x^2 - 1\}}_{=\frac{(R-R_m)^2}{R_m^2}}$$

Compare plot? shows that the potential are only in good agreement for $R \gtrsim R_m$ or $E \to E_{min} = -\varepsilon$, that is good for E_0 and maybe E_1 but not all E_n.

c) Numerical derivative for calculated physisorption potential for H_2/Cu(111):

$\delta z = 0.5$ Å gives $\Delta\varepsilon \approx 7$ meV (lower bound use ruler!)

Thus $k = m\omega_{vib}^2 \sim 56$ meV/Å^2

For H_2 the mass is $M = 2 \cdot 1.6726 \cdot 10^{-27}$ kg so this gives

$$\omega_{vib} \simeq 1.7 \cdot 10^{13}\ s^{-1}$$

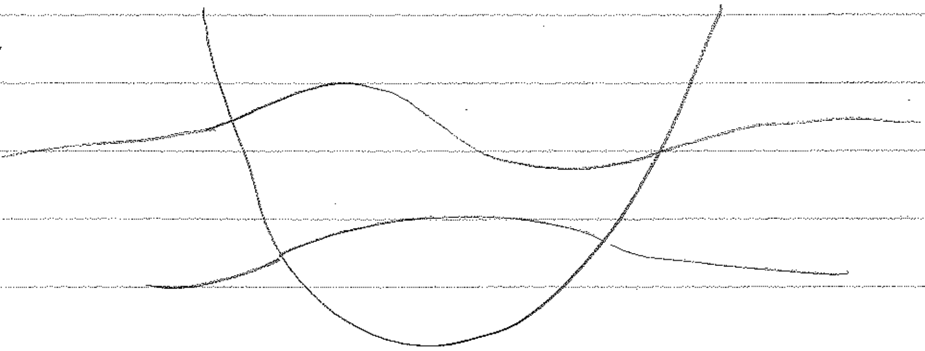
In turn we have $\hbar\omega_{vib} \simeq 11$ meV (for H_2) which should be compare to potential depth of ~35 meV.

- For D_2? Scale by $\frac{1}{\sqrt{2}}$ as twice the weight.

Problem III

a)

Sketch



$$H_a = \hbar\omega_{eff}\left(b^\dagger b + \tfrac{1}{2}\right) - \varepsilon_{eff}$$

b) Since

$$\hat{b} = \frac{m\omega_{eff}\,\hat{x} + i\hat{p}_y}{\sqrt{2\hbar m\omega_{eff}}}$$

$$\hat{b} + \hat{b}^\dagger = \hat{x}\left(\frac{2m\omega_{eff}}{\hbar}\right)^{1/2}$$

Thus

$$H_1(t) = \left(\frac{\hbar}{2m\omega_{eff}}\right)^{1/2}(-eE_{ext})\cos(\omega t)(\hat{b}+\hat{b}^\dagger)$$

c) First + second order effects at $\omega \ll \omega_{eff}$?
Steady state perturbation theory
(treating $\cos(\omega t)$ as a parameter)

Then

– firstorder shifts

$$E_0^{(1)} = \langle 0|H_1(t)|0\rangle \propto \langle 0|(\hat{b}+\hat{b}^\dagger)|0\rangle = 0$$

$$E_1^{(1)} = \langle 1|H_1(t)|1\rangle \propto \langle 1|(\hat{b}+\hat{b}^\dagger)|1\rangle = 0.$$

Second order

$$E_0^{(2)} = \sum_m \frac{\langle 0|H_1(t)|m\rangle\langle m|H_1(t)|0\rangle}{E_0^{(0)} - E_m^{(0)}}$$

$$= \frac{\langle 0|H_1(t)|1\rangle\langle 1|H_1(t)|0\rangle}{E_0^{(0)} - E_1^{(0)}}$$

because $(\hat{b}+\hat{b}^\dagger)|0\rangle$ exclusively has an overlap with $m=1$

Thus

$$E_0^{(2)} = -\frac{|\langle 0|\hat{b}|1\rangle|^2}{\hbar\omega_{eff}}\left(\frac{\hbar}{2m\omega_{eff}}\right)(eE_{ext})^2\cos^2\omega t$$

$$= -\frac{(eE_{ext})^2\cos^2(\omega t)}{2m\,\omega_{eff}^2}.$$

} also O.K. to give answer without "$\cos^2(\omega t)$".

d) Fermi's golden rule; $H_1(t) = H_1'\cos\omega t$

$$\Gamma_{0\to 1} = \left(\frac{2\pi}{\hbar}\right)|\langle 0|H_1'|1\rangle|^2\,\delta(\omega - \omega_{eff})$$

$$= \left(\frac{2\pi}{\hbar}\right)\left(\frac{\hbar}{2m\omega_{eff}}\right)(eE_{ext})^2\,\delta(\omega-\omega_{eff})$$

$$= \pi\frac{(eE_{ext})^2}{m\omega_{eff}}\,\delta(\omega-\omega_{eff})$$ (ignoring degeneracy

(Or "$\times\underbrace{\rho(E_1)}_{\text{DOS}}$" with degeneracy)

e) Two-atom model?

In normal coordinate $X = (x_1 + x_2)/\sqrt{2}$ and $Y = (x_1 - x_2)/\sqrt{2}$ we can consider

$$m\omega_{eff}^2 (X^2 + Y^2) = (x_1^2 + x_2^2)\, m\omega_{eff}^2$$

No cross-terms in X^2 or Y^2 contributes here. Next consider the contributions from

$$-\frac{1}{2} f_R X^2 + \frac{1}{2} f_R Y^2$$

Here it is only the crossterms that contributes, giving $-f_R x_1 x_2$, ie the interatomic term H'_R.

Consider next the momentum terms: we can define $\hat{P}_X = -i\hbar \frac{\partial}{\partial X}$ (and similarly for $\hat{p}_Y$) and then evaluate by the chain rule. For example

$$\frac{\partial}{\partial X} = \left(\frac{\partial x_1}{\partial X}\right)\frac{\partial}{\partial x_1} + \left(\frac{\partial x_2}{\partial X}\right)\frac{\partial}{\partial x_2}$$

Keeping track of the $1/\sqrt{2}$-factor it follows that $\hat{P}_X^2 + P_Y^2 = \hat{P}_{x_1}^2 + P_{x_2}^2$

and that

$$H_{2a} = \frac{P_X^2}{2m} + \frac{P_Y^2}{2m} + \frac{1}{2} m\left(\omega_{eff}^2 - \frac{f_R}{m}\right) X^2 + \frac{1}{2} m\left(\omega_{eff}^2 + \frac{f_R}{m}\right) Y^2$$

f) EvdW?

In essence the coupling H'_R gives us a new double-harmonic oscillator problem with new frequencies

$$\omega_1 = \sqrt{\omega_{eff}^2 - f_R/m} \quad \& \quad \omega_2 = \sqrt{\omega_{eff}^2 + f_R/m}.$$

In a ground state a single oscillator will have energy $\frac{1}{2}\hbar\omega$.

So $\langle H^0_{2a}\rangle_{GS} = 2 \cdot \frac{1}{2}\hbar\omega_{eff}$.

But $\langle H_{2a}\rangle = \frac{1}{2}\hbar(\omega_1 + \omega_2)$

$$E_{vdW} = \langle H_{2a}\rangle - \langle H^0_{2a}\rangle$$

$$= \frac{1}{2}\hbar\sqrt{\omega_{eff}^2 - f_R/m} + \frac{1}{2}\hbar\sqrt{\omega_{eff}^2 + f_R/m} - \hbar\omega_{eff}$$

$$= \frac{1}{2}\left(\frac{f_R}{m}\right)^2 \frac{1}{\omega_{eff}^3} \propto -1/R^6$$

Problem IV

a): Occupying 2 orbitals with 'n' electrons:

1: ε_0 ; 2: $2\varepsilon_0$ if ↑↓ but $(\varepsilon_0+\varepsilon_1)$ if ↑↑;

3: $2\varepsilon_0+\varepsilon_1$

b) $\theta(t) = (-i\varepsilon_0 t/\hbar)$ from SE.

SE gives

$$|\psi(t)\rangle = \exp(-i\varepsilon_0 t/\hbar)\,\alpha_0|0\rangle + \exp(-i\varepsilon_1 t/\hbar)\,\beta_0|1\rangle$$

so

$$c(t) = \beta_0 \exp(-i(\varepsilon_1-\varepsilon_0)t) = \beta_0 \exp(-i\omega_{osc} t)$$

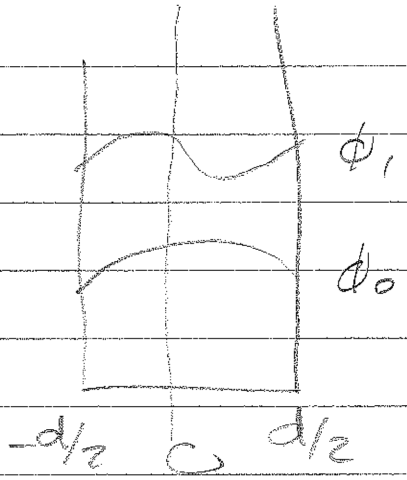
c) Probability ?

$$P_0(t) = |\langle\psi(t)|0\rangle|^2 = |\alpha_0|^2$$

$$P_1(t) = |\langle\psi(t|1\rangle|^2 = |\beta_0|^2$$

The energy 'probability' and expectation value does not itself oscillate.

c) Particle in a box



$\phi_0 = N_0 \cos\left(\frac{x\pi}{d}\right)$

$\phi_1 = N_1 \sin\left(\frac{2x\pi}{d}\right)$

The values of $N_0 N_1$ can be found in Physics handbook – but also OK to just leave that!!

$\langle x \rangle (t)$?

$\langle 0 | x | 0 \rangle = \langle 1 | x | 1 \rangle = 0$ by symmetry.

However

$$\langle 0 | x | 1 \rangle = N_0 N_1 \int_{-d/2}^{d/2} dx \cos\left(\frac{x\pi}{d}\right) x \sin\left(\frac{2x\pi}{d}\right)$$

$= D$ real.

So

$\langle x \rangle (t) = \langle \psi(t) | x | \psi(t) \rangle =$

$\alpha_0^* \cdot c(t) \langle 0 | x | 1 \rangle$

$+ \alpha_0 \cdot c^*(t) \langle 0 | x | 1 \rangle$

$= D \cos(\omega_{osc} t)$. | at $\alpha_0 = \beta_0 = 1/\sqrt{2}$.

Nature? the particle moves (oscillates) in space over time.

Next spin version of twolevel system:

In the homogeneous field there is just spin dynamics under

$$H_0 = \frac{\hbar\omega_{osc}}{2}\underline{\underline{\sigma}}_z + \left(\frac{\varepsilon_1+\varepsilon_0}{2}\right)\underline{\underline{1}}$$

The dynamics is just our

$$|\psi(t)\rangle = e^{i\theta(t)}\{\alpha_0|0\rangle + c(t)|1\rangle\}$$

At time $t=0$ and t_1 the beam is in two Stern Gerlach (SG) probes, having an inhomogeneous field. These sorts the beam, performing a measurement of whether the Ag atoms have spin up or spin down according to the SG field ∥ z-direction.

d+e) With a field in direction x the probabilities for sorting into either beam is given by matrix elelments

$$\langle\psi|\chi_{\uparrow x}\rangle \quad \text{and} \quad \langle\psi|\chi_{\downarrow x}\rangle$$

Hence we need to find eigenvectors of Pauli matrix $\underline{\underline{\sigma}}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

In the spinor notation given by our states $|0\rangle$ and $|1\rangle$ these eigen values satisfy

$$\chi_{\uparrow x}: \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = + \begin{pmatrix}\alpha\\ \beta\end{pmatrix} \longleftarrow \text{'}\chi_{\uparrow x}\text{'}$$

$$\chi_{\downarrow x}: \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = - \begin{pmatrix}\alpha\\ \beta\end{pmatrix} \longleftarrow \text{'}-\chi_{\downarrow x}\text{'!}$$

d) It is easy to see that

$|\psi(t=0)\rangle$ is just '$\chi_{\uparrow x}$'

for $\alpha_0 = \beta_0 = \frac{1}{\sqrt{2}}$.

— Hence the $|\psi(t=0)\rangle$ state is exactly ~~what characterize one~~ of the two beams leaving the first SG probe (when it has $\bar{B} \parallel x$-direction)

— Also for a general $|\psi(t=0)\rangle = \alpha_0|0\rangle + \beta_0|1\rangle$ we can always pick the direction $\hat{n}$ of the first SG B-field so that $|\psi(t=0)\rangle$ is exactly the state in one of the beam.

— practical approach? Simply allow just one beam to leave SG1.

⑭

e) When the state $|\psi(t=0)\rangle$ leaves SG1 it will evolve in time according to $H_0 = (\hbar\omega_{osc}/2)\sigma_z$ + const.

Note { This is not a measurement as the field is homogeneous and there will be no 'sorting' for $0<t<t_1$.

When it get to the second SG at time t_1 then the atoms will be sorted according to a probability given by the overlap of $|\psi(t_1)\rangle$ and $\chi_{\uparrow x}$ and $\chi_{\downarrow x}$.

Specifically

$$P^{SG2}_{\uparrow x} = |\langle \chi_{\uparrow x} | \psi(t)\rangle|^2$$

and

$$\langle \chi_{\uparrow x} | \psi(t)\rangle = \frac{1}{2} e^{i\theta(t)} (1 \ 1) \begin{pmatrix} 1 \\ e^{-i\omega_{osc}t} \end{pmatrix}$$

$$= \frac{1}{2}\left(1 + e^{-i\omega_{osc}t}\right) e^{i\theta(t)} \quad \text{For } \alpha_0 = \beta_0 = \frac{1}{\sqrt{2}}$$

$$= e^{i\theta(t)} \cdot e^{-i\omega_{osc}t/2} \cos(\omega_{osc}t/2)$$

- The probability for sorting is thus given (as a function of t_1) by $\cos^2(\omega_{osc}t/2)$ and $\sin^2(\omega_{osc}t/2)$.

— [illegible] Th [illegible] giving [illegible]

Nature of oscillation in spin system?

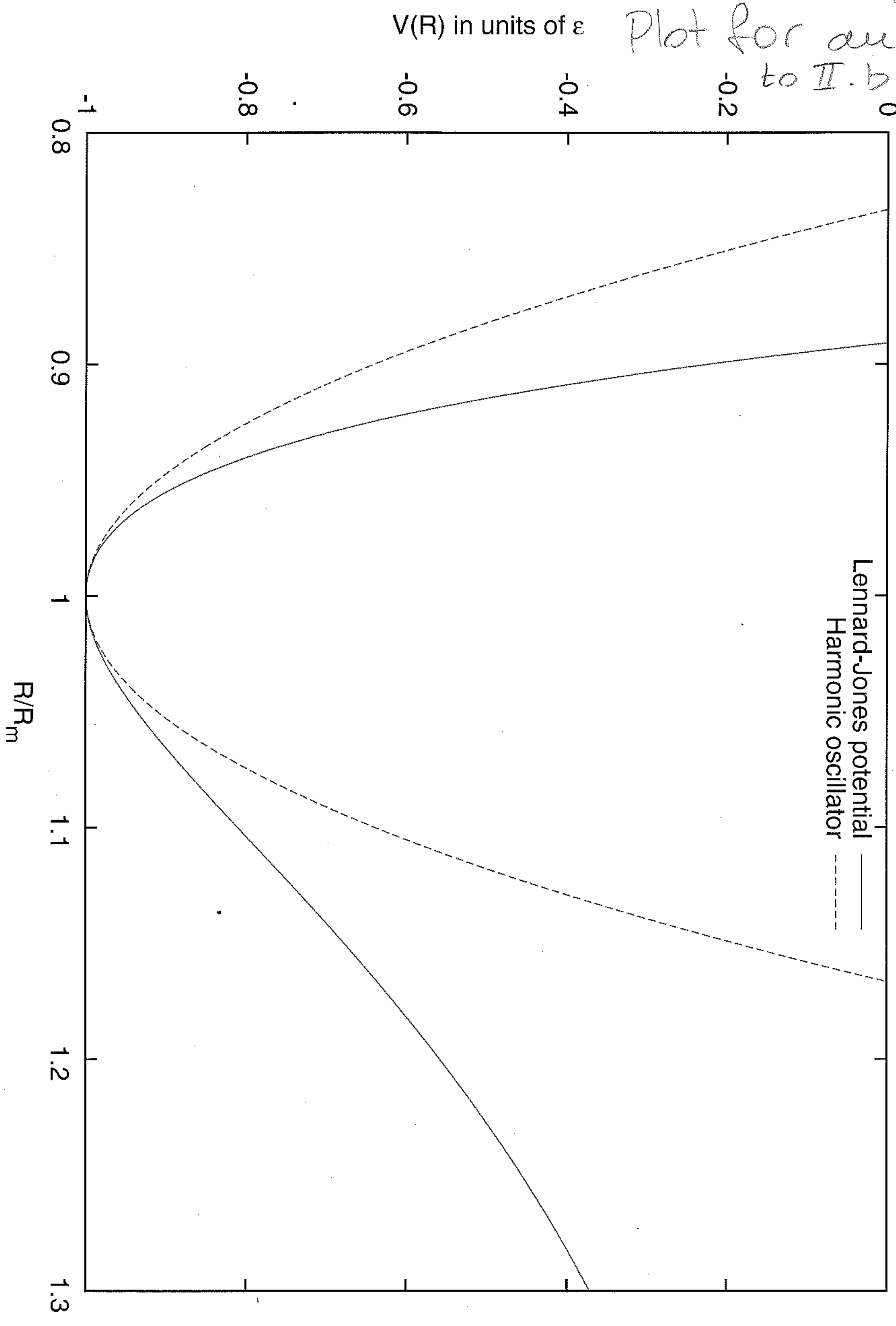
The homogeneous field at $0 < t < t_1$ drives a precission of the spin. The precission will not necessarily have completed an integer number of rotations when at t_1 we probe the spin alignment again.

Problem V

Please see separate sheet with answer to chemistry problems.

P 5A

Plot for answer to II.b.



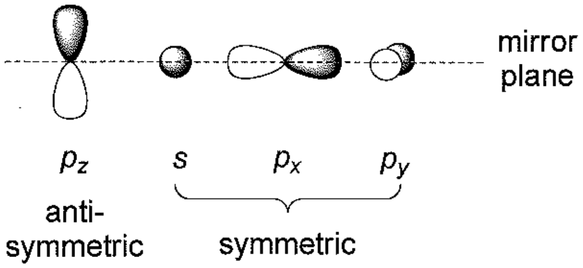
Answers to exam questions, 2016-10-26, Chemistry parts

Question I.e) What defines a bonding molecular orbital?

Answer: A bonding molecular orbit is lower in energy than any of the atomic orbitals from which it is derived.

Question I.f) One basic assumption in Hückel theory is that the atomic orbitals (p_z) contributing to the π-bonding in a planar molecule can be treated independently from the atomic orbitals contributing to the σ-bonding in the molecule. Why is this assumption valid?

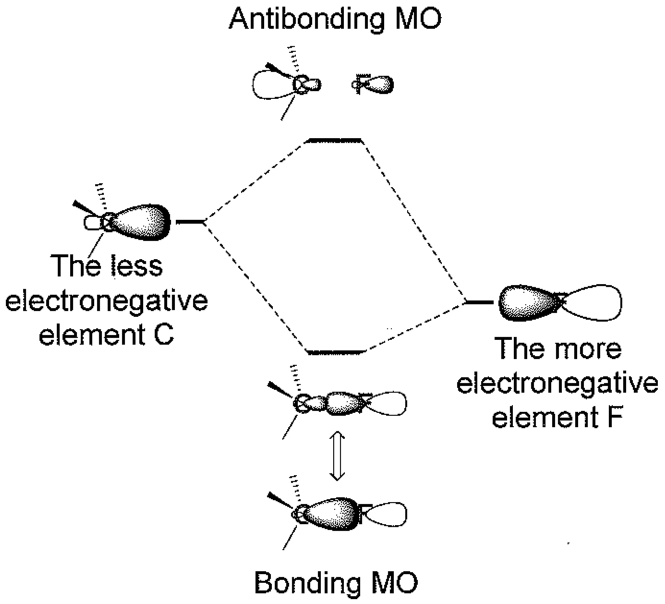
Answer: The net overlap between the atomic p-orbitals (p_z) perpendicular to the molecular plane with the atomic orbitals contributing (s, p_x And p_y) to the σ-bonding orbitals are zero. Another way to put it: the atomic p-orbitals (p_z) perpendicular to the molecular plane are of a different symmetry compared to the atomic orbitals (s, p_x And p_y) contributing to the σ-bonding.



Problem V: The polymer polytetrafluoroethylene (PTFE/Teflon) is a solid and is often used when a very nonreactive (stable) and "non-sticky" surfaces are needed. ...

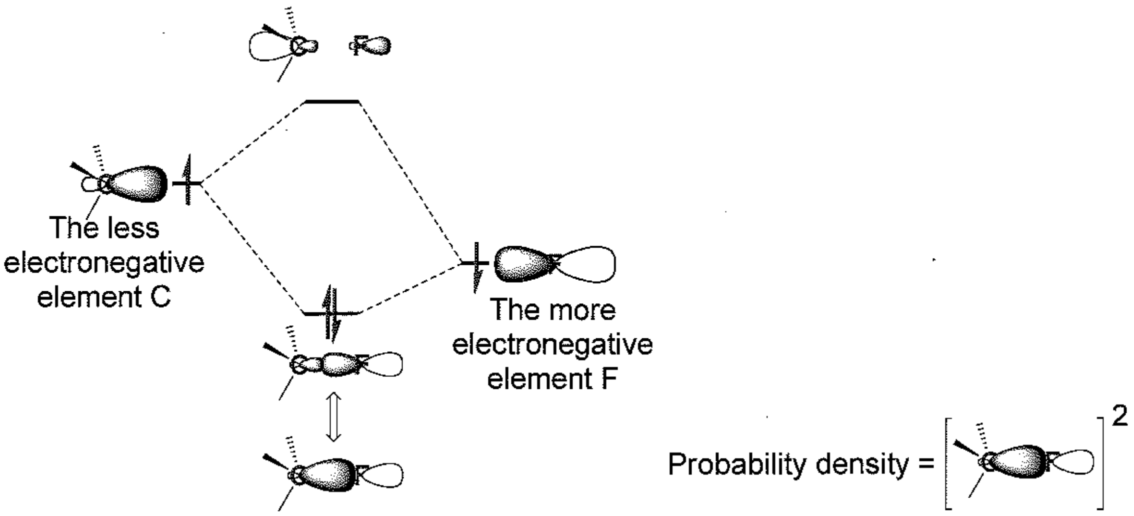
Question V.a) Draw an orbital interaction diagram showing the bonding and antibonding molecular orbitals (MOs) corresponding to a carbon-fluorine bond. Use a sp^3-orbital on the carbon atom and a p-orbital on the fluorine atom as the base (staring-point). (1 point)

Answer:



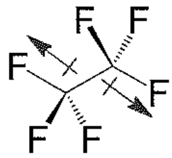
Question V.b) The carbon-fluorine is one of the strongest, if not the strongest, bond in organic chemistry. It is also one of the most polar covalent bonds. Use your orbital interaction diagram to show why the carbon-fluorine is a highly polarized bond. (1 point)

Answer: *The distribution of electrons are determined by the square of the wavefunction (the orbital). Only the bondning orbital is filled with electrons of the two molecular orbitals – the bondning and the antibonding molecular orbitals – shown in the diagram. The atomic orbital closer in energy compared to the molecular orbital makes a larger contribution of the two atomic orbitals used in the linear combination to construct the molecular orbital. The high electronegativity of fluorine is a consequence of the low energy of its atomic orbitals. Thus, the p-orbital on the fluorine makes a larger contribution to the bonding molecular orbital compared to the sp^3-orbital on the carbon. The orbital lobes will be "larger" around the fluorine atom compared to around the carbon. In consequence, the square of the bonding orbital shows that there is a higher probability of finding the bonding electrons closer to the fluorine compared to the carbon.*



Question V.c) Hexafluoroethane may be considered as a small model of Teflon. Does this molecule have a large or small dipole moment? (1 points)

Answer: Hexafluoroethane has no permanent dipole moment. The dipole moments of the individual bonds cancel and the resultant dipole moment of hexafluoroethane is zero.



Question V.d) Explain why Teflon is a "non-sticky" material. It is both hydrophobic and lipophobic, i.e. it does not shows substantial intermolecular interactions with neither polar compounds nor with non-polar compounds such as hydrocarbons ($C_xH_{(2x+2)}$). (3 points)

Answer: *Teflon is a non-polar material. For that reason, it cannot participate in intermolecular interactions with ions or molecules with permanent dipoles (Polar compounds). The carbon backbone of Teflon is shielded (covered) by fluorine atoms. The properties of Teflon is therefore largely determined by the properties of fluorine. Fluorine is a very small atom and has the highest electronegativity of all elements. Consequently, fluorine has the lowest polarizability of all* *elements. Due to the low polarizability, Teflon gives rise to very small London dispersion forces (instantaneous dipole–induced dipole forces). London forces are present between all chemical groups, and represent the main part of the total interaction force between non-polar (lipophilic) compounds. The interaction between Teflon and non-polar molecules (and others) are therefore very weak.*