

Exam
Quantum Engineering (FKA132), Chalmers
2017-08-15

Time and place: 8:00-12:00 on August 15, 2017, 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) Write down the time-independent Schrödinger equation and explain all terms of the equation. Assume that the time-independent Schrödinger equation has the set of eigenvalues $\{E_\alpha\}$ and eigenvectors $\{\psi_\alpha\}$. Write down the general solution $\psi(\mathbf{r}, t)$ to corresponding time-dependent Schrödinger equation, i.e., the solution to the quantum problem.

b) Oligoacenes are molecules in which multiple benzene rings are stringed together, one after another. Consider two examples, benzene C_6H_6 and anthracene $C_{14}H_{10}$ and assume that each C atom has a mass equal to 12 times the mass of a proton. Here we consider the dynamics of individual molecules, as dilute gases. If both types molecules are moving at kinetic energy given by the anthracene boiling point, $K_B T \approx 50$ meV, what are the de Broglie wavelengths of the benzenes and anthracenes? [1 point]

c) Assume that a^\dagger and a are creation and annihilation operators that, for example, describe a harmonic-oscillator system and satisfy $[a, a^\dagger] = 1$. Consider next an linear combination $d = \alpha a + \beta a^\dagger$ and evaluate $[d, d^\dagger]$. [1 point]

d) An harmonic oscillator (describing dynamics in direction x) is described in terms the annihilation operator

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\hat{x} + i\frac{\hat{p}_x}{\hbar}\right), \quad (1)$$

and the Hermitian conjugate creation operators \hat{a}^\dagger . Express the perturbation $\hat{H}_1(t) = C\hat{x}^2 \cos^2(\omega t)$ in terms of \hat{a} and \hat{a}^\dagger .

e) Define the concept “electronegativity”.

f) State the requirements needed to be fulfilled by a compound to be aromatic (not in the context of having an aroma but in the context of chemical bonding).

Problem 2. [6 points total]

A molecule of mass M moves in the potential

$$V(x) = V_0 \left\{ \tanh^2 \left(\frac{x}{a} \right) - 1 \right\} \quad (2)$$

where V_0 and a are positive constants.

a) What is the “best fit” harmonic oscillator approximation to this potential? That is, consider Taylor-expansion around the energy minimum and express the approximate harmonic-oscillator frequency Ω_0 in terms of V_0 , a , and the particle mass M .

b) What is the energy spectrum of the harmonic oscillator fit?

The set of normalized steady-state solutions $|n\rangle$ of the actual potential problem has energies ϵ_n (you do not have to compute these).

c) Sketch the wavefunctions for both the lowest- and second-lowest stationary states, assuming your harmonic-oscillator approximation is valid.

d) Sketch both the actual and the model potential, and discuss the quantitative differences that exists between the potentials when $|x| \gg a$.

e) For given values of a , V_0 , and M , up to what values of n (number in spectrum) is the harmonic oscillator spectrum a reasonable approximation?

f) Given the state $|\psi(t = 0)\rangle = \frac{1}{2}|2\rangle + \frac{1}{\sqrt{2}}|3\rangle + \frac{1}{C}|5\rangle$ at time $t = 0$. Determine C and describe the state change at $t > 0$ (write down $|\psi(t)\rangle$ for $t > 0$).

Problem 3. [6 points total]

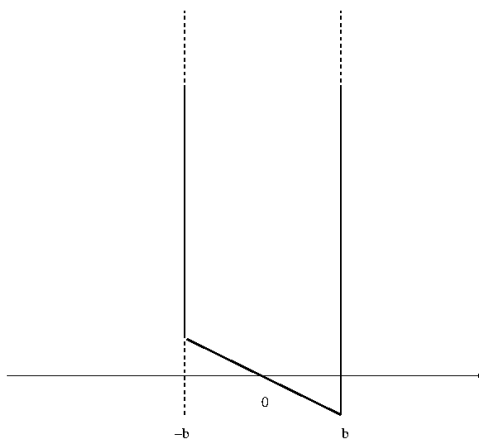


Figure 1: *Sketch of the potential $V(x)$ in problem 3.*

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

$$V(x) = \begin{cases} \infty & \text{for } x < -b \\ \eta \left(\frac{x}{b} \right) & \text{for } -b < x < b \\ \infty & \text{for } b < x \end{cases} \quad (3)$$

where $\eta < 1$ is a small energy. The potential is illustrated in Fig. 1.

a) Argue that it is useful to split the problem into an unperturbed starting system \hat{H}_0 and a perturbation term $\hat{H}_1 \equiv \eta(x/b)$, when you can also assume that η is small compared to the ground-state energy.

b) Calculate the eigenenergy for the lowest state of the system given above to first order in the perturbation \hat{H}_1 .

It may be useful to use the ‘Extra resources’ at the end.

c) Compute the energy shift of the ground state to second order, assuming that we can focus exclusively on the contribution from the coupling between the lowest two eigenstates.

It may be useful to use the ‘Extra resources’ at the end.

d) Assume that we irradiate the system at a frequency ω so that $\hbar\omega$ is close to the energy difference between the first and second level, $\hbar\omega \approx E_2 - E_1$; this irradiation is described by the time-dependent perturbation

$$\delta\hat{H}(t) = (e E_{\text{rad}}^0) \hat{x} \cos(\omega t). \quad (4)$$

Provide a formal Fermis golden-rule estimate of the rate of transition from the ground to first excited state.

Problem 4. [6 points total]

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

$$\hat{H} = -\frac{1}{\mu_0} \boldsymbol{\mu} \cdot \mathbf{B}, \quad \boldsymbol{\mu} = -\frac{g\mu_B}{2} \boldsymbol{\sigma} \quad (5)$$

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 electron spinors.

b) At time $t = 0$ the electron is in its spin-up state, relative to the z -axis. Describe the time evolution of the spin state of the electron at $t > 0$, i.e., the spin wavefunction as a function of time, $\chi(t)$.

c) Calculate the probabilities of finding the electron in the spin-down state, $P_{\downarrow}(t)$, (seen relative to direction z), as a function of the time $t > 0$.

d) Consider finally the dynamics of two electrons moving under the influence of the spin Hamiltonian \hat{H} . Assume that the electrons occupy the same eigenstate of the Hamiltonian for the spatial wavefunction and ignore all physical interactions between the electrons. If one electron is measured to be in a spin-down configuration at $t = t_1$, what is the probability distribution for finding the other electron in spin up or spin down configurations at time $t_2 > t_1$?

Problem 5. [6 points total]

Fluoride gas has the molecular formula F₂.

- a) Draw a correct Lewis structure for this compound. [1 point]
- b) Construct and draw a molecular orbital energy level diagram for F₂ (the interaction between the two 2p-orbitals along the bond axis is much larger than between those perpendicular to this axis). [2 points]
- c) For each energy level, give a simple (omit constants) expression for the linear combination of atomic orbitals (AOs) that gives the best approximation of the corresponding molecular orbital (MO). [1 point]
- d) Correlate each bonding electron pair and free electron pair, if any, shown in your Lewis structure for F₂ with the correct linear combination of atomic orbitals (LCAOs) constructed in question c. [2 points]

Extra resources

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

$$\begin{aligned}\sin(2y) &= 2 \sin(y) \cos(y) \\ \int \sin^2(y) dy &= \frac{y}{2} - \frac{\sin(2y)}{4y} \\ \int \cos^2(y) dy &= \frac{y}{2} + \frac{\sin(2y)}{4y} \\ \int y \sin^2(y) dy &= \frac{y^2}{4} - \frac{y}{4} \sin(2y) - \frac{1}{8} \cos(2y). \\ \int y \cos^2(y) dy &= \frac{y^2}{4} + \frac{y}{4} \sin(2y) + \frac{1}{8} \cos(2y). \\ \int y \cos(y) \sin^2(y) dy &= \frac{1}{9} \left[-3y \cos^3(y) + \cos^2(y) \sin(y) + 2 \sin(y) \right].\end{aligned}$$

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Problem 1 /

a) Schrödinger equation (SE)

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H} \psi(\vec{r}, t)$$

is given by Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}, t)$$

where first term is kinetic energy and second term is a potential.

Time-independent Schrödinger equation is (mostly) relevant for time-independent potential $V(\vec{r})$, and given as the eigenvalue problem

$$\hat{H} \psi_{\alpha}(\vec{r}) = E_{\alpha} \psi_{\alpha}(\vec{r})$$

For a given (energy) eigenvector $\psi_{\alpha}(\vec{r})$ the actual (time-dependent) SE has the solution

$$\psi_{\alpha}(\vec{r}, t) = \psi_{\alpha}(\vec{r}) e^{-iE_{\alpha}t/\hbar}$$

b) Oligoacenes vs Benzene

Benzene has mass $M=78 m_p$
 Anthracene has mass $M=178 m_p$

Where proton mass m_p is ~ 2000 times electron mass m_e

Boiling point $E_{kin} \approx 50 \text{ meV}$ ($\approx 600 \text{ K}$)

Molecule momentum $p = \sqrt{2m E_{kin}}$

Note $(m_e \cdot Ry)^{1/2} = \frac{\hbar}{\sqrt{2} a_0} = \frac{h}{2\sqrt{2}\pi a_0}$; a_0 Bohr radius $\approx 0.529177 \text{ \AA}$

de Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{h}{(m_e Ry)^{1/2} \sqrt{2} \sqrt{\frac{M \cdot E_{kin}}{m_e Ry}}}$$

$= 2\pi a_0 \left\{ \begin{array}{l} 1/24.0 \text{ Benzene} \\ 1/36.2 \text{ Anthracene} \end{array} \right.$

Benzene has de Broglie wavelength $\sim 0.14 \text{ \AA}$
 Anthracene has de Broglie wavelength $\sim 0.09 \text{ \AA}$

c) $d = \alpha a + \beta a^\dagger$ means $d^\dagger = \alpha^* a^\dagger + \beta^* a$

$$[d, d^\dagger] = \alpha [a, a^\dagger] \alpha^* + \beta [a^\dagger, a] \beta^* = |\alpha|^2 - |\beta|^2$$

d)

$$a = \frac{1}{\sqrt{2}} \left(\hat{x} + i \frac{\hat{p}_x}{\hbar} \right)$$

$$a^\dagger = \frac{1}{\sqrt{2}} \left(\hat{x} - i \frac{\hat{p}_x}{\hbar} \right)$$

so $(a + a^\dagger) = \sqrt{2} \hat{x}$ and

$$\hat{x}^2 = \frac{1}{2} (a + a^\dagger)^2$$

Thus perturbation $\hat{H} = \frac{C}{2} \cos^2(\omega t) (a + a^\dagger)^2$

e) + f) See separate solutions for chemistry problems.

Problem 2/

Potential $V(x) = V_0 \left\{ \tanh^2\left(\frac{x}{a}\right) - 1 \right\}$

$\tanh(y)$ has a good linear behavior inside $-0.5 < y < 0.5$ and a fair linearity inside

$-\frac{1}{\sqrt{2}} < y < \frac{1}{\sqrt{2}}$; In this regime we may expand

$$\tanh^2\left(\frac{x}{a}\right) - 1 \approx \left(\frac{x}{a}\right)^2$$

a) Best fit harmonic potential is thus

$$V(x) \approx V_h(x) \equiv \frac{1}{2} K \cdot x^2 - V_0; \quad K = 2V_0/a^2$$

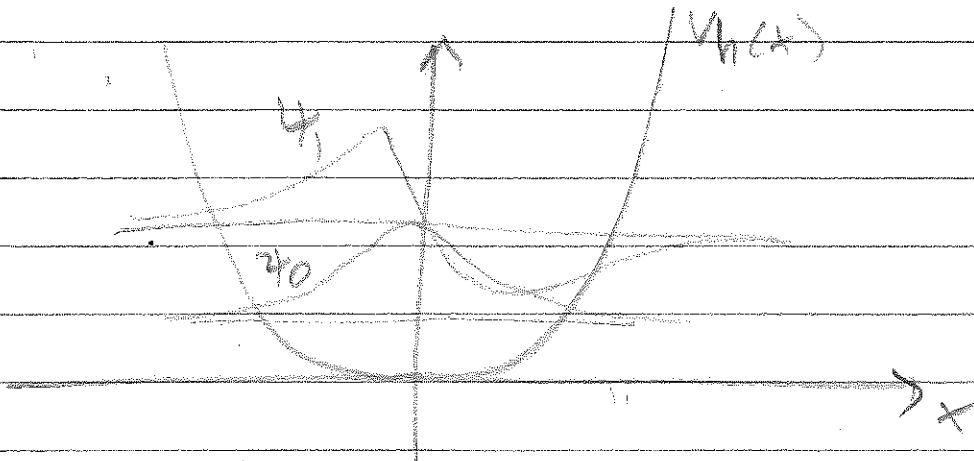
Approximate potential frequency is

$$\omega_0 = \sqrt{K/M} = \sqrt{\frac{2V_0}{Ma^2}}$$

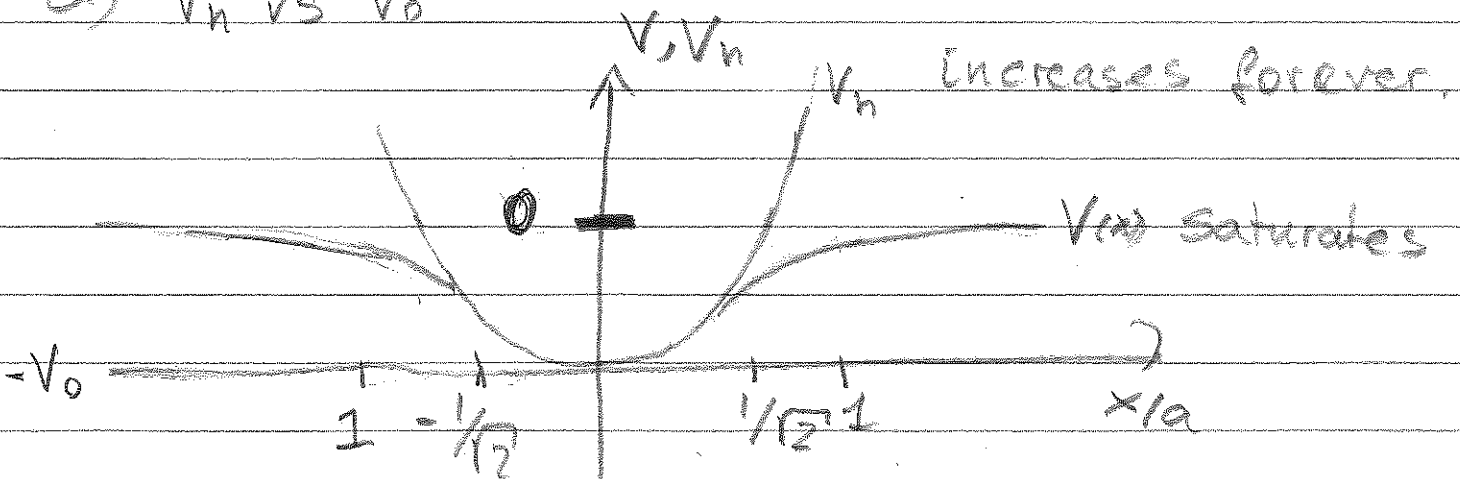
b) Energy spectrum (as 1D harmonic oscillator)

$$E_n = \hbar \omega_0 (n + 1/2), \quad n = 0, 1, \dots$$

c)



d) V_h vs V_0



e) Model breakdown when energy eigenvalue $E_n = \hbar \omega_0 (n + 1/2)$ exceeds V_0 (to keep it simple)

Thus criteria is

$$\hbar \omega_0 (2n + 1) < 2V_0 \iff$$

$$n \leq \frac{V_0}{\hbar \omega_0} - 1 = \frac{1}{\hbar} \frac{\sqrt{M a^2 V_0}}{\sqrt{2}}$$

f) State $| \psi(t=0) \rangle = \frac{1}{2} | 2 \rangle + \frac{1}{\sqrt{2}} | 3 \rangle + \frac{1}{2} | 5 \rangle$

Orthonomal states means

$$\langle m | n \rangle = \delta_{m,n}$$

Thus normalization means

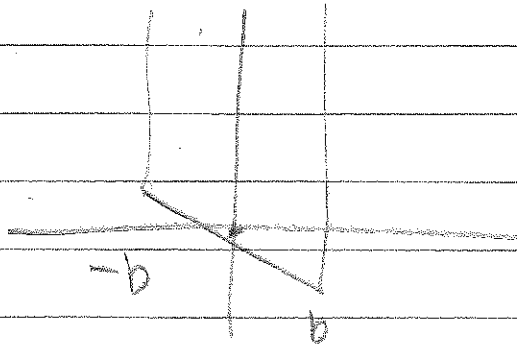
$$\langle \psi(t=0) | \psi(t=0) \rangle = \frac{1}{4} + \frac{1}{2} + \frac{1}{4} = 1$$

or $|C| = 2$; $C = 2 \cdot e^{i\alpha}$

Also

$$\begin{aligned} | \psi(t>0) \rangle &= \frac{1}{2} e^{-i(2+1/2)\omega_0 t} | 2 \rangle \\ &+ \frac{1}{\sqrt{2}} e^{-i(3+1/2)\omega_0 t} | 3 \rangle \\ &+ \frac{e^{-i\alpha}}{2} e^{-i(5+1/2)\omega_0 t} | 5 \rangle. \end{aligned}$$

(6)

Problem 3

a) Split:

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V_0, \quad H_1 = \gamma \left(\frac{x}{b} \right) \text{ for } -b < x < b$$

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

is use for proceeding by perturbation theory, noting that γ is small compare to ground-state energy.

$$E_1^0 = \frac{\hbar^2}{2m} \frac{\pi^2}{(2b)^2} \quad (\text{as described by } H_0 \text{ Hamiltonian})$$

b) First-order perturbation theory

$\delta E_1^{(1)} = \langle \psi_1 | H_1 | \psi_1 \rangle$ where \hat{H}_0 ground-state eigenvector $|\psi_1\rangle$ is given

$$\begin{aligned} \psi_1(x) &= \langle x | \psi_1 \rangle = \sqrt{\frac{2}{2b}} \sin\left(\frac{\pi(x+b)}{2b}\right) \\ &= \frac{1}{\sqrt{b}} \cos\left(\frac{\pi x}{2b}\right). \end{aligned}$$

$$\delta E_1^{(1)} = \frac{\eta}{b} \int_{-b}^b dx \left(\frac{x}{b}\right) \cdot \cos^2\left(\frac{\pi x}{2b}\right)$$

$$= \eta \int_{-1}^1 dy \cdot y \cdot \cos^2\left(\frac{\pi}{2} \cdot y\right) = 0$$

$$\text{So } E_1 \approx E_1^0 + E_1^{(1)} = E_1^0 = \frac{\pi^2 \hbar^2}{8m b^2}$$

c) Second order perturbation theory assuming we can focus on coupling to first excited state

$$E_2 = \frac{1}{2} \frac{\pi^2 \hbar^2}{m b^2} ; \psi_2(x) = \frac{1}{b} \sin\left(\frac{\pi x}{b}\right)$$

$$\delta E_1^{(2)} = \sum_{n \geq 1} \frac{|\langle \psi_1 | H_1 | \psi_n \rangle|^2}{E_1^0 - E_n^0}$$

$$\approx -\frac{1}{3} \cdot \frac{8m b^2}{\pi^2 \hbar^2} |\langle \psi_1 | H_1 | \psi_2 \rangle|^2$$

We need matrix element

$$\langle \psi_1 | (x/b) | \psi_2 \rangle = \int_{-b}^b dx \left(\frac{x}{b}\right) \frac{1}{b} \sin\left(\frac{\pi x}{b}\right) \cos\left(\frac{\pi x}{2b}\right)$$

$$= \int_{-1}^1 dy \cdot y \cdot \sin(\pi y) \cos(\pi y/2) \quad \begin{matrix} z = \pi y/2 \\ y = \frac{2z}{\pi} \end{matrix}$$

$$= \left(\frac{2}{\pi}\right)^2 \cdot 2 \int_{-\pi/2}^{\pi/2} dz \cdot z \cdot \sin(z) \cos^2 z$$

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$$= \left(\frac{2}{\pi}\right)^2 \cdot \frac{2}{9} \left[-32 \cos^3(z) + \sin z \cos^2 z + 2 \sin z \right]_{-\pi/2}^{\pi/2}$$

$$= \frac{8}{9} \left(\frac{2}{\pi}\right)^2$$

Thus change is approximately

$$\delta E_1^{(2)} \approx -\frac{1}{3} \frac{8 \pi b^2}{\pi^2 \hbar^2} \cdot \frac{1}{2} \cdot \left(\frac{32}{9\pi}\right)^2$$

d) $\delta \hat{H}_1(t) = C \cdot \hat{x} \cos(\omega t)$; $C = e E_{rad}$
 Time-dependent perturbation theory, Fermi golden rule

$$\gamma_{1 \rightarrow 2} = \frac{\pi}{2\hbar^2} |\langle \psi_1 | C \cdot \hat{x} | \psi_2 \rangle|^2 \delta(\omega - \omega_{12})$$

where $\hbar \omega_{12} = E_2^0 - E_1^0$

But we know the matrix elements already

$$\gamma_{1 \rightarrow 2} = \frac{\pi}{2\hbar^2} (e E_{rad} b)^2 \cdot \left[\frac{8}{9} \left(\frac{2}{\pi}\right)^2 \right]^2 \delta(\omega - \omega_{12})$$

(9)

Problem 4/

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

Spin Hamiltonian

$$\hat{H} = -\frac{1}{N_0} \vec{N} \cdot \vec{B} \quad ; \quad \vec{N} = \frac{g \mu_B}{2} \vec{\sigma} \quad ; \quad g \approx 2$$

Thus

$$\hat{H} \approx B_0 \frac{\mu_B}{N_0} \hat{\sigma}_x = \left(\frac{\mu_B}{N_0} \right) B_0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Use

$$\chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

to denote states with spin up/down in z direction.
Then eigenvalue problem is

$$B_0 \frac{\mu_B}{N_0} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \chi_n = E_n \chi_n, \quad n=0,1$$

for

$$\chi_n = \alpha \chi_{\uparrow} + \beta \chi_{\downarrow}$$

a) Orthonormal

Solutions are then

$$\chi_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{of energy } E_0 = -B_0 \frac{\mu_B}{N_0}$$

$$\chi_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{of energy } E_1 = B_0 \frac{\mu_B}{N_0}$$

$$\text{Let } J_B = (B_0 \frac{\mu_B}{N_0}) / \hbar$$

(10)

$$b) \chi(t=0) = \chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_{\uparrow} = \frac{1}{\sqrt{2}} (\chi_0 + \chi_1)$$

Thus

$$\chi(t) = \frac{1}{\sqrt{2}} \chi_0 e^{+i\Omega_B t}$$

$$+ \frac{1}{\sqrt{2}} \chi_1 e^{-i\Omega_B t}$$

$$= \begin{pmatrix} \cos(\Omega_B t) \\ -i \sin(\Omega_B t) \end{pmatrix}$$

$$= \cos(\Omega_B t) \chi_{\uparrow} - i \sin(\Omega_B t) \chi_{\downarrow}$$

$$c) P_{\downarrow}(t) = |\sin(\Omega_B t)|^2 \text{ oscillating}$$

d) Two electrons in same spatial-wave function state (but non interacting) then they must have opposite spin-directions.

If one is spin down at t_1 the other is spin up at $t = t_1$. Probability for spin down at $t' > t_1$ is then given by 'c':

$$P_{\downarrow}(t') = P_{\downarrow}(t' - t_1) = |\sin(\Omega_B(t' - t_1))|^2$$

Answers to exam questions August 2017

Problem 1.e) Define the concept “electronegativity”.

Answer

A measure of the ability of an atom in a chemical compound to attract electrons from another atom in the compound.

Problem 1.f) State the requirements needed to be fulfilled by a compound to be aromatic (not in the context of having an aroma but in the context of chemical bonding).

Answer

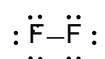
The molecule must contain:

- a. A continuous and cyclic conjugated system*
- b. The conjugated system must be planar*
- c. The number of electrons within the conjugated system must be $4n + 2$, where n is an integer including 0.*

Problem 5) Fluoride gas has the molecular formula F_2 .

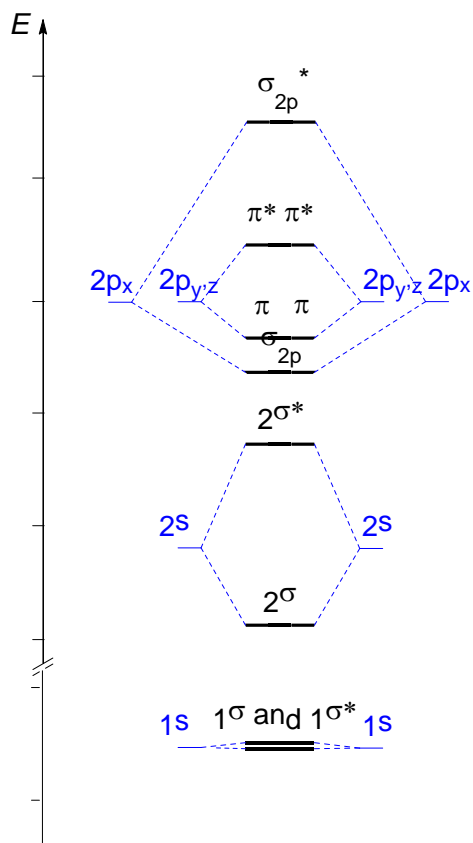
- a. Draw a correct Lewis structure for this compound. (1)

Answer



- b. Construct and draw a molecular orbital energy level diagram for F_2 (the “interaction between the two 2p-orbitals” along the bond axis is much larger than between those perpendicular to this axis). (2)

Answer



- c. For each energy level, give a simple (omit constants) expression for the linear combination of atomic orbitals (AOs) that gives the best approximation of the corresponding molecular orbital (MO). (1)

Answer

$$\sigma_{2p}^* \propto 2p_x - 2p_x$$

$$\pi^* \propto 2p_z - 2p_z$$

The same for $2p_y$

$$\pi \propto 2p_z + 2p_z$$

The same for $2p_y$

$$\sigma_{2p} \propto 2p_x + 2p_x$$

$$2\sigma^* \propto 2s - 2s$$

$$2\sigma \propto 2s + 2s$$

$$2\sigma^* \propto 1s - 1s$$

$$1\sigma \propto 1s + 1s$$

- d. Correlate each bonding electron pair and free electron pair, if any, shown in your Lewis structure for F_2 with the correct linear combination of atomic orbitals (LCAOs) constructed in question c. (2)

Answer

The Lewis structure of F_2 contains one σ -bond. The only filled bonding σ -orbital that is not counteracted by a filled anti-bonding σ -orbital is $\sigma_{2p} \propto 2p_x + 2p_x$. Thus, this corresponds to the σ -bond.

Only valence electrons are shown in Lewis structures. Thus, there are no electrons highlighted in the Lewis structure that correspond to the linear combinations of $1s$.

Therefore, the other linear combinations are represented as free electron pairs in the Lewis structure of F_2 .