CH932: Introduction to Chemistry and Biochemistry

Quantum Chemistry

Workshop

Name: ____________________

Date: ____________________

Problems

A table of the relevant physical constants can be found in the last page of this document. All the necessary formula can be found within the lecture notes (available on Moodle).

1. **de Broglie wavelength**

   A What is the de Broglie wavelength of a baseball moving at a speed $v = 10$ m/sec? Assume the mass of said baseball is 1.0 Kg.

   B What is the de Broglie wavelength of an electron whose kinetic energy ($K = \frac{p^2}{2m}$) is 100 eV? Note that 1 eV = $1.60218{\cdot}10^{-19}$ J [Joule ([Kg]$\cdot$[m]$^2\cdot$[s]$^{-2}$)].

   C Which of the two objects (baseball and electron) would display any evidence of wave-like motion? Why?

2. **(Quantum, or not) Harmonic Oscillator**
   Consider a particle of mass m bound in the harmonic oscillator potential:

$$V(x) = \frac{k}{2}x^2 \tag{1}$$

   where k is the force constant of the corresponding linear (along the direction x) restoring force.

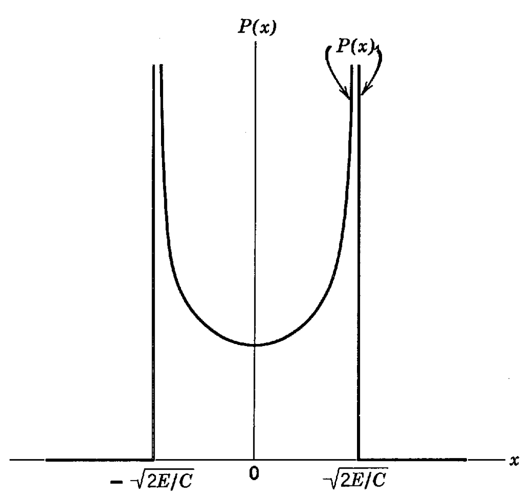
   A Write down the time-dependent Schröedinger equation describing the system.

   B Evaluate the probability density for the wave function corresponding to the lowest energy state of the quantum harmonic oscillator potential:

$$\psi(x,t) = Ae^{-\left(\frac{\sqrt{km}}{2\hbar}\right)x^2} \cdot e^{-\left(\frac{i}{2}\right)\sqrt{\frac{k}{m}}t}, \tag{2}$$

   where A is an arbitrary constant. Remember that the complex conjugate of a complex exponential is obtained by reversing the sign of the i appearing in the exponent.

   C Sketch the functional form of the resulting probability density and compare it against the probability density for the *classical* harmonic oscillator (illustrated in the figure below). Describe the differences (if any...) between the quantum and classical harmonic oscillator in terms of their probability densities.



Probability density for a particle in the lowest energy state of a *classical* harmonic oscillator.

3. **The Helium Atom**

The helium (He) atom contains two electrons bound to a nucleus containing two protons (hence the atomic number Z is equal to two). As a first approximation, we can try to calculate the energy levels of He by *ignoring the Coulomb interaction between the two electrons.* In this scenario, then, the total energy E_{He} of the He atom can be written as:

$$E_{\text{He, no Coul.}} = E_1^{e^-} + E_2^{e^-} \quad (3)$$

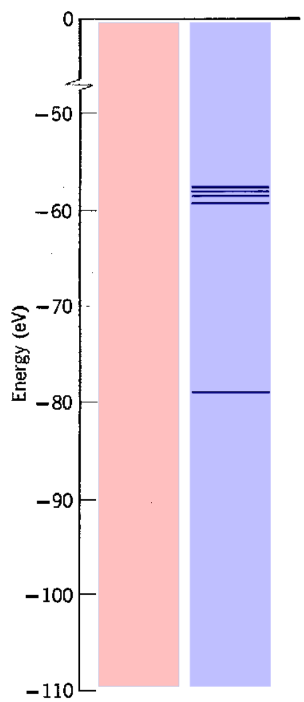
where the energy $E_i^{e^-}$ of the $i-th$ electron is just the one-electron atom energy, that is:

$$E_i^{e^-} = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n_i^2}, \quad (4)$$

where μ, e, $1/(4\pi\epsilon_0)$ and $\hbar$ are the reduced mass, the electron charge, the Coulomb's law constant and the Dirac constant respectively and the quantum number n_i indicates in which energy level (e.g. ground state n_i=1) the electron can be found.

A. Calculate the energies (in eV) of the ground and the excited state, keeping in mind that a Joule ([Kg]·[m]^2·[s]$^{-2}$) is equal to $6.242 \cdot 10^{18}$ eV.

B. Sketch the resulting energy levels within the red-shaded region in the figure below, which contains in the blue-shaded region the experimental values. Describe the differences (if any...) between the calculated and experimental results.

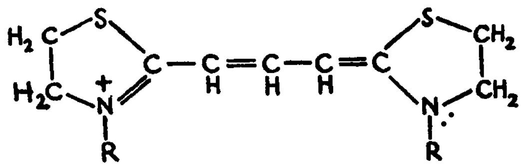


Helium energy levels, as determined from experimental measurements of the optical spectrum emitted by that atom.

4. **From Structure to Colour**

Consider the symmetrical polymethine dye depicted in the figure below.

A. The figure below illustrates one of the two resonant structures. Draw the other one.



Polymethine dye (cation, one resonant structure only).

B Would the particle in a box model be a reasonable approximation in order to describe the electronic structure of this molecule? Why?

C How many electrons are involved in the conjugate system? Note that the lone pair on the nitrogen atom must be included in the count.

D Sketch a diagram of the molecular electronic states of this molecule considering the N_c conjugated electrons only.

E The Highest Occupied Molecular Orbital (HOMO) contains $(N_c/2)$ electrons, so that we can assign to it a "quantum number" $n_{\text{HOMO}} = (N_c/2)$. What would be the expression for n_{LUMO} (where LUMO stands for the Lowest Unoccupied Molecular Orbital)?

F Within the particle in the box model, an electronic transition from the i energy level to the j energy level can be written as:

$$\Delta E_{i-j} = \frac{h^2}{8 m_e L^2} \cdot (n_j^2 - n_i^2), \tag{5}$$

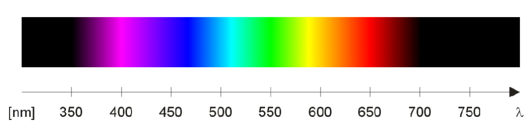
where m_e, L and n_j are the electron mass, the length of the box and the quantum number associated by the energy level j respectively. Write down the expression for $\Delta E_{\text{HOMO-LUMO}}$.

G What is the length L of the "box"? Note that the average length of a C-C double bond is 1.39 Å, and that in order to include the lone pairs of the nitrogen atoms and additional bond length has to be added - for each N at the end of the conjugated chain. Assume that the average length of a N-C double bond is also 1.39 Å.

H The electronic transition from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) is characterised by a wavelength:

$$\lambda_{\text{HOMO-LUMO}} = \frac{hc}{\Delta E_{\text{HOMO-LUMO}}}. \tag{6}$$

What is the colour of this dye in solution? The visible region of the electromagnetic spectrum is depicted in the figure below.



The visible region of the electromagnetic spectrum.

Physical Constants

Constant	Symbol	Value
Planck's constant	h	$6.6 \cdot 10^{-34}$ J $\cdot$ s
Reduced mass	$\mu \approx m_e$	$9.109 \cdot 10^{-31}$ Kg
Electron mass	m_e	$9.109 \cdot 10^{-31}$ Kg
Electron charge	e	$1.602 \cdot 10^{-19}$ C
Coulomb's law constant	$\frac{1}{4\pi\epsilon_0}$	$8.988 \cdot 10^{9}$ N$\cdot$ m^2 $\cdot$ C^{-2}
Dirac constant	$\hbar$	$1.055 \cdot 10^{-34}$ J $\cdot$ s
Speed of light in vacuum	c	$2.998 \cdot 10^{8}$ m$\cdot$ s

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Answer Key for Exam A

Problems

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   C Which of the two objects (baseball and electron) would display any evidence of wave-like motion? Why?

   Answer: A

$$\lambda = \frac{h}{p} = \frac{6.6 \cdot 10^{-34} \text{ J} \cdot \text{s}}{1.0 \text{ Kg} \cdot 10 \text{ m/s}} = 6.6 \cdot 10^{-35} \text{ m} = 6.6 \cdot 10^{-25} \text{ Å}$$

   B

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e K}} = \frac{6.6 \cdot 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2 \cdot 9.1 \cdot 10^{-31} \text{ Kg} \cdot 100 \text{ eV} \cdot 1.6 \cdot 10^{-19} \text{ J/eV}}} = 1.2 \cdot 10^{-10} \text{ m} = 1.2 \text{ Å}$$

   C The electron, as its de Broglie wavelength is such to allow for e.g. diffraction effects to take place.

2. **(Quantum, or not) Harmonic Oscillator**
   Consider a particle of mass m bound in the harmonic oscillator potential:

$$V(x) = \frac{k}{2}x^2 \tag{1}$$

   where k is the force constant of the corresponding linear (along the direction x) restoring force.

   A Write down the time-dependent Schröedinger equation describing the system.

   B Evaluate the probability density for the wave function corresponding to the lowest energy state of the quantum harmonic oscillator potential:

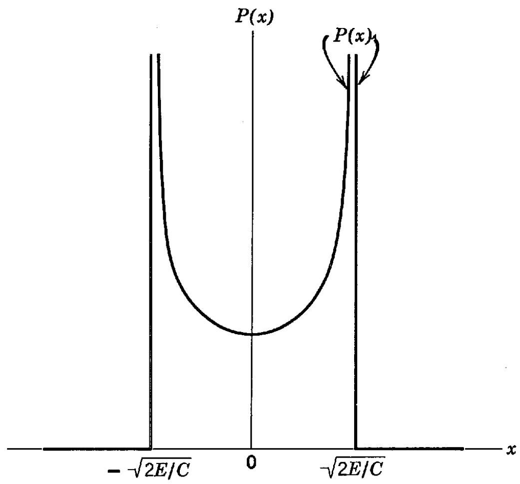
$$\psi(x,t) = Ae^{-\left(\frac{\sqrt{km}}{2\hbar}\right)x^2} \cdot e^{-\left(\frac{i}{2}\right)\sqrt{\frac{k}{m}}t}, \tag{2}$$

   where A is an arbitrary constant. Remember that the complex conjugate of a complex exponential is obtained by reversing the sign of the i appearing in the exponent.

   C Sketch the functional form of the resulting probability density and compare it against the probability density for the *classical* harmonic oscillator (illustrated in the figure below). Describe the differences (if any...) between the quantum and classical harmonic oscillator in terms of their probability densities.

   Answer: A

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + \frac{k}{2}x^2\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

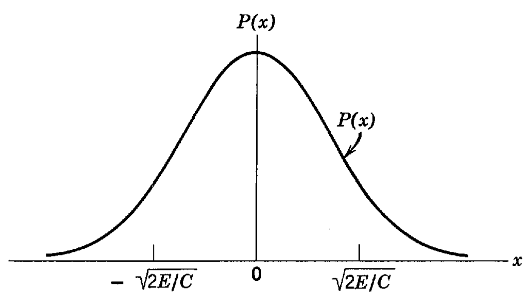


Probability density for a particle in the lowest energy state of a *classical* harmonic oscillator.

B

$$\begin{aligned} P &= \psi(x,t)^* \cdot \psi(x,t) = Ae^{-\left(\frac{\sqrt{km}}{2\hbar}\right)x^2} \cdot e^{+\left(\frac{i}{2}\right)\sqrt{\frac{k}{m}}t} \cdot Ae^{-\left(\frac{\sqrt{km}}{2\hbar}\right)x^2} \cdot e^{-\left(\frac{i}{2}\right)\sqrt{\frac{k}{m}}t} \\ &= A^2 e^{-\left(\frac{\sqrt{km}}{\hbar}\right)x^2} \end{aligned}$$

C Probability density for a particle in the lowest energy state of a *quantum* harmonic oscillator. The classical and the quantum case differ dramatically. In the quantum case, the probability of finding the particle is maximum at the equilibrium point of the oscillator, while in the classical case the probability is at his maxima near the limits of its motion (remember, we are talking about the lowest energy state). Speaking of which, in the quantum case there are no well-defined limits beyond which the particle will never be found.



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The helium (He) atom contains two electrons bound to a nucleus containing two protons (hence the atomic number Z is equal to two). As a first approximation, we can try to calculate the energy levels of He by *ignoring the Coulomb interaction between the two electrons.* In this scenario, then, the total energy E_{He} of the He atom can be written as:

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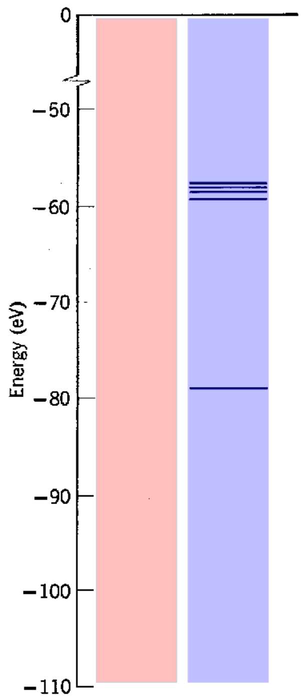
where μ, e, $1/(4\pi\epsilon_0)$ and $\hbar$ are the reduced mass, the electron charge, the Coulomb's law constant and the Dirac constant respectively and the quantum number n_i indicates in which energy level (e.g. ground state n_i=1) the electron can be found.

A Calculate the energies (in eV) of the ground and the excited state, keeping in mind that a Joule ([Kg]·[m]^2·[s]$^{-2}$) is equal to 6.242·10^{18} eV.

B Sketch the resulting energy levels within the red-shaded region in the figure below, which contains in the blue-shaded region the experimental values. Describe the differences (if any...) between the calculated and experimental results.



Helium energy levels, as determined from experimental measurements of the optical spectrum emitted by that atom.

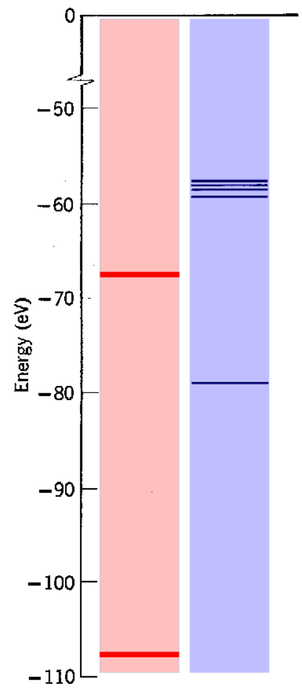
Answer: A In the ground state, the quantum numbers n_1 and n_2 for electrons 1 and 2 are both equal to 1. Hence:

$$
\begin{aligned}
E_{\text{He, no Coul.}}^{\text{Ground state}} &= E_1^{e^-} + E_2^{e^-} \\
&= -\frac{\mu 4 e^4}{(4\pi\epsilon_0)^2\hbar^2} \\
&= -\frac{9.109\cdot 10^{-31}\ \text{Kg}\cdot 4\cdot(1.602\cdot 10^{-19}\ \text{C})^4\cdot(8.988\cdot 10^9\ \text{N}\cdot\text{m}^2\cdot\text{C}^{-2})^2}{(1.055\cdot 10^{-34}\ \text{J}\cdot\text{s})^2} \\
&= -108.72\ \text{eV}
\end{aligned}
$$

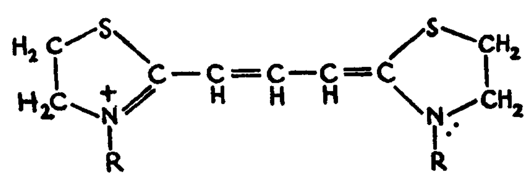
In the first excited state n_1=1 and n_2=2 (or, equivalently, the other way around, being indistinguishable particles), so that:

$$
\begin{aligned}
E_{\text{He, no Coul.}}^{1^{st}\text{ exc. state}} &= E_1^{e^-} + E_2^{e^-} \\
&= -\frac{\mu 2 e^4}{(4\pi\epsilon_0)^2\hbar^2} - \frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2} = -\frac{\mu 4 e^4}{(4\pi\epsilon_0)^2\hbar^2}\cdot\frac{5}{8} = -67.95\ \text{eV}
\end{aligned}
$$

B The calculated energy levels are utterly wrong, because the Coulomb interaction between the two electrons is *not* negligible with respect to the Coulomb interaction between each electron and the nucleus. The experimental energy levels are higher in energy than the calculated ones because the Coulomb interaction between the two electrons has a positive sign (the electrons have the same, negative charge). In addition to this, the first excited state is split in two (well, four, but let's start with two). This is because the two electrons are characterised by another (on top of n) quantum number l which is related to their angular momentum. The first excited state splits into two because we can have $l_1 = l_2 = 0$ and $l_1 = 0 \neq l_2 = 1$. Finally, each of those two states can be a singlet or a triplet (i.e. different spin states), so that leads to four energy levels for the first excited state of the helium atom.



4. **From Structure to Colour**
Consider the symmetrical polymethine dye depicted in the figure below.



Polymethine dye (cation, one resonant structure only).

A The figure below illustrates one of the two resonant structures. Draw the other one.

B Would the particle in a box model be a reasonable approximation in order to describe the electronic structure of this molecule? Why?

C How many electrons are involved in the conjugate system? Note that the lone pair on the nitrogen atom must be included in the count.

D Sketch a diagram of the molecular electronic states of this molecule considering the N_c conjugated electrons only.

E The Highest Occupied Molecular Orbital (HOMO) contains $(N_c/2)$ electrons, so that we can assign to it a "quantum number" $n_{\text{HOMO}} = (N_c/2)$. What would be the expression for n_{LUMO} (where LUMO stands for the Lowest Unoccupied Molecular Orbital)?

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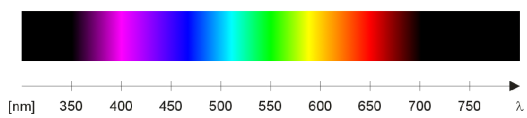
where m_e, L and n_j are the electron mass, the length of the box and the quantum number associated by the energy level j respectively. Write down the expression for $\Delta E_{\text{HOMO-LUMO}}$.

G What is the length L of the "box"? Note that the average length of a C-C double bond is 1.39 Å, and that in order to include the lone pairs of the nitrogen atoms and additional bond length has to be added - for each N at the end of the conjugated chain. Assume that the average length of a N-C double bond is also 1.39 Å.

H The electronic transition from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) is characterised by a wavelength:

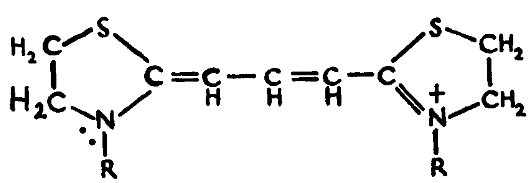
$$\lambda_{\text{HOMO-LUMO}} = \frac{hc}{\Delta E_{\text{HOMO-LUMO}}}. \tag{6}$$

What is the colour of this dye in solution? The visible region of the electromagnetic spectrum is depicted in the figure below.



The visible region of the electromagnetic spectrum.

Answer: A The second resonant structure of the dye is depicted in the figure below.

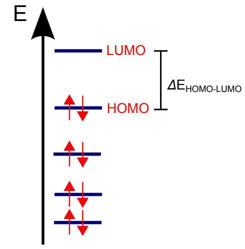


B The particle in a box model would be indeed a reasonable approximation for this system, as the π electrons involved in the C-C double bonds (as well as the lone pair on the nitrogen atom) are basically delocalized across the whole length of the conjugated chain. The resulting potential is thus quite similar to that of the particle in the box problem.

C We have 3 double bonds and 1 lone pair. Each one of these involves two electrons, so in total we have 8.

D A diagram of the molecular electronic states of this molecule considering the N_c conjugated electrons only is sketched below.

E $\frac{N_c}{2} + 1$. The LUMO is just one energy level away from the HOMO.



F

$$
\begin{aligned}
\Delta E_{\text{HOMO-LUMO}} &= \frac{h^2}{8m_eL^2}\cdot(n^2_{\text{LUMO}}-n^2_{\text{HOMO}}) \\
&= \frac{h^2}{8m_eL^2}\cdot\left[\left(\frac{N_c}{2}+1\right)^2-\left(\frac{N_c}{2}\right)^2\right] \\
&= \frac{h^2}{8m_eL^2}\cdot(N_c+1)
\end{aligned}
$$

G From one nitrogen atom to the other one (basically from the start to the end of the conjugated chain) we have 6 C-C (or C-N) double bonds. Adding two C-N double bonds (one for each N at the ends of the conjugated chain) leads to 8 bonds. As each one of those has an average length of 1.39 Å, the length of the box (i.e. the dimension of the conjugated system) is $1.39x8 = 11.12$ Å.

H

$$
\begin{aligned}
\lambda_{\text{HOMO-LUMO}} &= \frac{hc}{\Delta E_{\text{HOMO-LUMO}}} \\
&= \frac{hc}{h^2\cdot(N_c+1)}8m_eL^2 = \frac{c8m_eL^2}{h\cdot(N_c+1)} \\
&= \frac{2.998\cdot10^8\ \text{m}\cdot\ \text{s}\cdot8\cdot9.1\cdot10^{-31}\ \text{Kg}\cdot(11.12\text{Å})^2}{6.6\cdot10^{-34}\ \text{J}\cdot\text{s}\cdot9} \\
&= 454\cdot10^9\ \text{m} = 454\ \text{nm, which correspond to a beautiful blue}
\end{aligned}
$$

Note that the experimental value of $\lambda_{\text{HOMO-LUMO}}$ for this very molecule is 445 nm [(see e.g. J. Chem. Phys. **17**, 1198 (1949)]. Not too bad an achievement for the humble particle in a box model!

Physical Constants

Constant	Symbol	Value
Planck's constant	h	$6.6 \cdot 10^{-34}$ J $\cdot$ s
Reduced mass	$\mu \approx m_e$	$9.109 \cdot 10^{-31}$ Kg
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Speed of light in vacuum	c	$2.998 \cdot 10^{8}$ m$\cdot$ s