

The 6 π -electrons of benzene can be modeled as independent, free particles on a ring with a radius of 134 pm. The Hamiltonian for a π -electron is $-\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2}$.

1. What are the boundary conditions satisfied by the solutions to the Schrödinger equation? [5]
2. What are the solutions to the Schrödinger equation satisfying the boundary condition in 1? [5]
3. Write the energies of the three lowest levels and identify the quantum numbers of the states in these levels. [5]
4. According to this model, at what wavelength (in nm) does the lowest energy absorption occur? ($m_e = 9.109 \times 10^{-31}$ kg, $h = 6.626 \times 10^{-34}$ J s $^{-1}$, $c = 3.0 \times 10^8$ m s $^{-1}$) [10]

An electron in H-atom is in the state $\psi(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos \theta$.

5. Plot ψ as a function of z . [5]
6. Find $\langle x \rangle$. Information you might need: $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ [10]
7. What is the most probable radius? [5]
8. In this state, what is the orbital angular momentum and its z -projection? [5]

Two electrons are confined on a square sheet with a unit positive charge fixed in the center.

9. Write the Hamiltonian for the system. [10]
10. Do you expect the solution to the Schrödinger equation to be of the form $\psi(x_1, y_1, x_2, y_2) = \phi_1(x_1, y_1)\phi_2(x_2, y_2)$? Why or why not? [5]

Consider the molecule, H_3^+ , composed of three protons (A , B , and C) and one electron with the protons at the corners of an equilateral triangle.

11. Write down the complete Hamiltonian for this system in atomic units. [5]
12. A possible LCAO MO for the system is $\psi = c(1s_A + 1s_B + 1s_C)$, where $1s_A$, $1s_B$, and $1s_C$ denote the normalized H-atom $1s$ state at A , B , and C respectively. Normalize ψ . What is the physical significance of the integrals that appear in your expression? [10]
13. Decide, with a justification, whether ψ is a bonding or antibonding MO. Marks only if the justification is correct. [5]
14. Obtain an expression for the approximate energy of ψ . Use standard notation for the integrals. Which of these integrals is responsible for bond formation? [15]

The 6 π -electrons of benzene can be modeled as independent, free particles on a ring with a radius of 134 pm. The Hamiltonian for a π -electron is $-\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2}$.

1. What are the boundary conditions satisfied by the solutions to the Schrödinger equation? [5]

Answer: The boundary condition is $\psi(\phi) = \psi(\phi + 2\pi)$.

No partial marking

2. What are the solutions to the Schrödinger equation satisfying the boundary condition in 1? [5]

Answer: We need to solve

$$-\frac{\hbar^2}{2mr^2} \frac{d^2\psi}{d\phi^2} = E\psi$$

We rewrite this as

$$\frac{d^2\psi}{d\phi^2} + k^2\psi = 0,$$

where $k^2 = \frac{2mr^2E}{\hbar^2}$.

The solutions of this differential equation that satisfy the boundary condition in the answer to question 1 are

$$\psi = Ae^{ik\phi},$$

where $k = 0, \pm 1, \pm 2, \dots$ are the possible quantum numbers.

Alternate answer:

$$\psi = Ae^{ik\phi} + Be^{-ik\phi}$$

where $k = 0, 1, 2, \dots$.

Alternate answer:

$$\psi = A \sin(k\phi) + B \cos(k\phi)$$

where $k = 0, \pm 1, \pm 2, \dots$.

Four marks for the solution and one mark for the allowed values of k . Partial marking: Two marks if the Schrödinger equation is correct and two marks for the solution. Definition of k should be correct.

3. Write the energies of the three lowest levels and identify the quantum numbers of the states in these levels. [5]

Answer: The energies are obtained from the definition $k^2 = \frac{2mr^2E_k}{\hbar^2}$. The lowest level has $k = 0$ with zero energy. The second level has $k = \pm 1$ (two-fold degeneracy) with energy $\frac{\hbar^2}{2mr^2} = \frac{h^2}{8\pi^2mr^2} = \frac{h^2}{8\pi^2I}$. The third level with quantum number $k = \pm 2$ has energy $\frac{4\hbar^2}{2mr^2} = \frac{h^2}{2\pi^2mr^2} = \frac{h^2}{2\pi^2I}$.

Partial marking: One mark for each correct energy and quantum state. Two marks if only energies are correct. Two marks if only quantum states are correct.

4. According to this model, at what wavelength (in nm) does the lowest energy absorption occur? ($m_e = 9.109 \times 10^{-31} \text{ kg}$, $h = 6.626 \times 10^{-34} \text{ J s}^{-1}$, $c = 3.0 \times 10^8 \text{ m s}^{-1}$) [10]

Answer: There are six π -electrons, which would fill the $k = 0$ and $k = \pm 1$ states. The HOMO is $k = \pm 1$ and LUMO is $k = \pm 2$. Hence, the wavelength of light would correspond to absorption from the second level to the third level. That is,

$$\frac{hc}{\lambda} = \frac{3\hbar^2}{2mr^2}$$

$$\lambda = \frac{4\pi mcr^2}{3\hbar} = \frac{4 \times 3.1415 \times 9.109 \times 10^{-31} \text{ kg} \times 3.0 \times 10^8 \text{ m s}^{-1} \times (134 \times 10^{-12} \text{ m})^2}{3 \times 1.054 \times 10^{-34} \text{ J s}^{-1}}$$

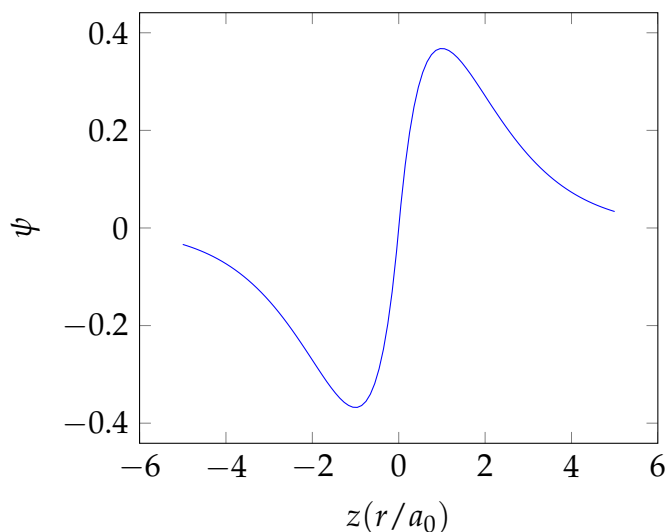
$$\lambda = 195 \text{ nm}$$

Marking scheme

- Three marks for distributing the electrons correctly.
- Two marks for noting that ΔE corresponds to transition from second to third level.
- Two marks for correct ΔE or λ expression.
- Three marks for correct numerical value, including unit.

An electron in H-atom is in the state $\psi(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta$.

5. Plot ψ as a function of z . [5]



Answer: Three marks if graph is one-sided.

6. Find $\langle x \rangle$. Information you might need: $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ [10]

Answer:

$$\langle x \rangle = \int \psi^* x \psi d\tau = \int \psi^* (r \sin\theta \cos\phi) \psi d\tau$$

$$\frac{1}{16\pi a_0^3} \int_0^\infty \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} r^3 dr \int_0^\pi \cos^2 \theta \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi$$

$$\langle x \rangle = \frac{1}{16\pi a_0^3} \int_0^\infty e^{-\frac{r}{a_0}} r^5 dr \int_0^\pi \cos^2 \theta \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi$$

The integral over ϕ is zero and as a result $\langle x \rangle = 0$.

Two marks for writing the correct expression for $\langle x \rangle$. Two marks each for writing the form of the r -, θ - and ϕ -integral correctly. Two marks for final answer.

7. What is the most probable radius? [5]

Answer: Most probable radius is obtained by solving

$$\frac{d\left(Ar^2\left(r^2e^{-\frac{r}{a_0}}\right)\right)}{dr} = 0 = e^{-\frac{r}{a_0}}\left(4r^3 - \frac{r^4}{a_0}\right)$$

Note that the constants and the angular part are unimportant and denoted as A . The most probably radius is $r = 4a_0$.

Two marks for noting that r_{mp} is obtained by solving for r from $\frac{d(r^2R^2)}{dr} = 0$. Two marks for correct derivative. One mark for answer.

8. In this state, what is the orbital angular momentum and its z -projection? [5]

Answer: The state has $l = 1$ and $m = 0$. The orbital angular momentum is $\sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$ and its z -projection is $m\hbar = 0$.

One mark for writing correct expression for orbital angular momentum. One mark for correct expression for z -projection. One mark each for identifying l and m correctly.

Two electrons are confined on a square sheet with a unit positive charge fixed in the center.

9. Write the Hamiltonian for the system. [10]

Answer: If the electron coordinates are (x_1, y_1) and (x_2, y_2) , the distance from electron 1 to the origin is r_1 , from electron 2 to the origin is r_2 , and that between the two electrons is r_{12} , we have

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Or

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0 \sqrt{x_1^2 + y_1^2}} - \frac{e^2}{4\pi\epsilon_0 \sqrt{x_2^2 + y_2^2}} + \frac{e^2}{4\pi\epsilon_0 \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}}$$

Or

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Or

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 \sqrt{x_1^2 + y_1^2}} - \frac{e^2}{4\pi\epsilon_0 \sqrt{x_2^2 + y_2^2}} + \frac{e^2}{4\pi\epsilon_0 \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}}$$

Expanding $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ is not required. Replacing $\frac{e^2}{4\pi\epsilon_0} = k$ or 1 is acceptable. Signs are important.

Two marks for each correct term.

10. Do you expect the solution to the Schrödinger equation to be of the form $\psi(x_1, y_1, x_2, y_2) = \phi_1(x_1, y_1)\phi_2(x_2, y_2)$? Why or why not? [5]

Answer: No. The presence of the last term, the inter-electronic repulsion term, which is a function of two electron coordinates, does not allow the separation of the Hamiltonian into the sum of two parts. Or alternatively, if $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, then $\psi = \phi_1\phi_2$.

One mark for Yes/No. Keywords: inter-electronic repulsion, two-electron coordinates, separability

Consider the molecule, H_3^+ , composed of three protons (A, B, and C) and one electron with the protons at the corners of an equilateral triangle.

11. Write down the complete Hamiltonian for this system in atomic units. [5]

Answer:

$$\hat{H} = -\frac{1}{2m_A} \nabla_A^2 - \frac{1}{2m_B} \nabla_B^2 - \frac{1}{2m_C} \nabla_C^2 - \frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} - \frac{1}{r_C} + \frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}}$$

No marks if atomic units are not used. Three marks if the nuclear kinetic energies are missing or wrong. Two marks if the nuclear repulsions are missing or wrong. Two marks if the signs of the potential energy terms are wrong.

12. A possible LCAO MO for the system is $\psi = c(1s_A + 1s_B + 1s_C)$, where $1s_A$, $1s_B$, and $1s_C$ denote the normalized H-atom $1s$ state at A, B, and C respectively. Normalize ψ . What is the physical significance of the integrals that appear in your expression? [10]

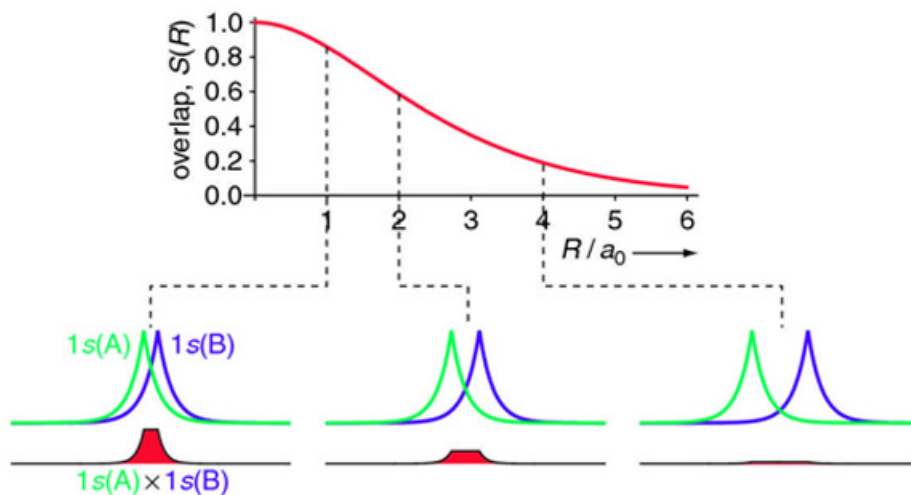
Answer:

$$\int |\psi|^2 d\tau = 1 = \int c^2(1s_A + 1s_B + 1s_C)(1s_A + 1s_B + 1s_C) d\tau$$

Denoting $\int 1s_A 1s_B d\tau = S_{AB}$ and similarly for the other integrals

$$\int |\psi|^2 d\tau = 1 = c^2(1 + S_{AB} + S_{AC} + S_{BA} + 1 + S_{BC} + S_{CA} + S_{CB} + 1)$$

Because the molecule is an equilateral triangle all the overlap integrals are equal, S. Hence we get $c^2 3(1 + 2S) = 1$ or $c = \frac{1}{\sqrt{3(1+2S)}}$.



The integrals are called overlap integrals and is a measure of the overlap between the atomic orbitals on two different atoms. It is large when the distance between the atoms is small and decreases with increasing distance.

Three marks if the function is correctly normalized. No marks deducted if all the overlap integrals are different.

13. Decide, with a justification, whether ψ is a bonding or antibonding MO. Marks only if the justification is correct. [5]

Answer: The state ψ is a bonding state. We find terms like $2s_A s_B$ in $|\psi|^2$ which is indicative of constructive interference and hence in increased electron density in the region between the nuclei. This leads to a bonding force.

Key ideas: Constructive interference, increased electron density between the nuclei

14. Obtain an expression for the approximate energy of ψ . Use standard notation for the integrals. Which of these integrals is responsible for bond formation? [15]

Answer: We work within the Born-Oppenheimer approximation - the nuclei are fixed.

$$E = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi \psi d\tau}$$

Two marks

$$E(3(1 + 2S)) = \int 1s_A \hat{H} 1s_A d\tau + \int 1s_A \hat{H} 1s_B d\tau + \int 1s_A \hat{H} 1s_C d\tau + \int 1s_B \hat{H} 1s_A d\tau + \int 1s_B \hat{H} 1s_B d\tau + \int 1s_B \hat{H} 1s_C d\tau + \int 1s_C \hat{H} 1s_A d\tau + \int 1s_C \hat{H} 1s_B d\tau + \int 1s_C \hat{H} 1s_C d\tau$$

Two marks

$$E = \frac{H_{AA} + H_{AB} + H_{AC} + H_{BA} + H_{BB} + H_{BC} + H_{CA} + H_{CB} + H_{CC}}{3(1 + 2S)}$$

Two marks

$$\begin{aligned}
 H_{AA} &= \int 1s_A \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) 1s_A d\tau + \\
 &\quad \int 1s_A \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) 1s_A d\tau + \\
 &\quad \int 1s_A \left(\frac{-1}{r_B} \right) 1s_A d\tau + \int 1s_A \left(\frac{-1}{r_C} \right) 1s_A d\tau \\
 &= E_H(1s) + \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + J_{AB} + J_{AC}
 \end{aligned}$$

where $J_{AB} = \int 1s_A \frac{-1}{r_B} 1s_A d\tau$ is the Coulomb integral. Similar expressions may be written for H_{BB} and H_{CC} by analogy.

$$H_{BB} = E_H(1s) + \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + J_{BA} + J_{BC}$$

$$H_{CC} = E_H(1s) + \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + J_{CA} + J_{CB}$$

Three marks if any of these expressions are correct. If the expression is incorrect, but the Coulomb integral is identified correctly, one mark.

$$\begin{aligned}
 H_{AB} &= \int 1s_A \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_B} \right) 1s_B d\tau + \\
 &\quad \int 1s_A \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) 1s_B d\tau + \\
 &\quad \int 1s_A \left(\frac{-1}{r_A} \right) 1s_B d\tau + \int 1s_A \left(\frac{-1}{r_C} \right) 1s_B d\tau \\
 &= SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{ABA} + K_{ABC}
 \end{aligned}$$

where two kinds of exchange integrals are defined $K_{ABA} = \int 1s_A \left(\frac{-1}{r_A} \right) 1s_B d\tau$ and $K_{ABC} = \int 1s_A \left(\frac{-1}{r_C} \right) 1s_B d\tau$ Expressions may be written for the other 5 terms by analogy.

$$H_{AC} = SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{ACA} + K_{ACB}$$

$$H_{BA} = SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{BAB} + K_{BAC}$$

$$H_{BC} = SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{BCB} + K_{BCA}$$

$$H_{CA} = SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{CAC} + K_{CAB}$$

$$H_{CB} = SE_H(1s) + S \left(\frac{1}{r_{AB}} + \frac{1}{r_{AC}} + \frac{1}{r_{BC}} \right) + K_{CBC} + K_{CBA}$$

Three marks if any of these expressions are correct. The term responsible for bonding are the exchange integrals K .

Three marks if the form of the exchange integral is correct and identified as the term responsible for bonding.