Physical Chemistry
A Guided Inquiry

Atoms, Molecules, and Spectroscopy

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Hückel Molecular Orbitals
(Is HMO a health management organization?)

Although the Schrödinger equation can be written for molecules, the equation cannot be solved. Various approximation methods can be used to deal with our inability to solve the Schrödinger equation, and these methods differ greatly in the degree of sophistication and the need for known experimental values as parameters.

Most of these approximation methods have several connections to the hydrogen atom.

- The atomic orbitals (ao) on the atoms within the molecule are the one-electron atomic orbitals of the hydrogen. (For example, the atomic orbitals for the carbon atom are the 1s, 2s, and 2p one-electron orbitals.)

- These methods involve overlap of the atomic orbitals of the atoms within the molecule as the basis of the electron sharing (which reduces the nuclear/nuclear repulsion) and bond formation.

- These methods are, fundamentally, one-electron approximations. That is, these methods generate a one-electron molecular orbital (mo) energy diagram (note that the solution to the hydrogen atom generates a one-electron ao diagram). Then, the number of electrons in the molecule are placed into the one-electron mo energy diagram (similar to the placement of the electrons for multielectron atoms into the one-electron ao diagram for the hydrogen atom).

These are very severe approximations, and you might conclude that the results would be well off the mark. However, by including the values for known quantities (IEs, electronegativities, heats of formation, and so on) as parameters in semi-empirical equations some very useful information can be obtained.

One of the simplest approximation methods, and one that demonstrates many of the characteristics of more complicated methods, is known as the Hückel Molecular Orbital (HMO) method.
Model 1: The $\pi$-bond in Ethylene/HMO.

\[ \text{H} \quad \text{C}_1 \equiv \text{C}_2 \quad \text{H} \]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

$2p$ orbital on carbon 1 = $p_1 \quad p_2 = 2p$ orbital on carbon 2

The classical expression for the energy and the Hamiltonian operator are never explicitly written in the HMO method. Furthermore, the trial wave function is written as a linear combination of atomic orbitals, LCAO, that comprise the $\pi$ system. For ethylene, we use the $2p$ orbitals normal to the plane of the molecule.

\[ \Psi_{\text{trial}} = c_1 p_1 + c_2 p_2 \quad (1) \]

$p_1 = \Psi_{2p}$ on atom 1 (the $2p$ orbital normal to the plane of the molecule)

$p_2 = \Psi_{2p}$ on atom 2 (the $2p$ orbital normal to the plane of the molecule)

Only one-electron is described by $\Psi_{\text{trial}}$.

The coefficients $c_1$ and $c_2$ are constants, but their values are unknown at this point.

Now, the expression for the average value of the energy can be written:

\[ \langle \varepsilon \rangle = \frac{\int \Psi_{\text{trial}}^* \hat{H} \Psi_{\text{trial}} d\tau}{\int \Psi_{\text{trial}}^* \Psi_{\text{trial}} d\tau} \quad (2) \]
Critical Thinking Questions

1. The two carbon nuclei repel each other. What location of an electron is most conducive to bond formation: when an electron is to the left of carbon 1; when an electron is between carbon 1 and carbon 2; when an electron is to the right of carbon 2? Explain.

2. In the HMO method, what is the trial function for the \( \pi \)-system of 1,3-butadiene?

Exercise

1. Write the HMO trial function for the \( \pi \)-system of benzene.

Information

The expression for the average value of the energy, equation (2) can be expanded:

\[
\langle \varepsilon \rangle = \frac{\int \Psi_{\text{trial}}^{\ast} \hat{H} \Psi_{\text{trial}} d\tau}{\int \Psi_{\text{trial}}^{\ast} \Psi_{\text{trial}} d\tau} = \frac{\int (c_{1} p_{1}^{\ast} + c_{2} p_{2}^{\ast}) \hat{H} (c_{1} p_{1} + c_{2} p_{2}) d\tau}{\int (c_{1} p_{1}^{\ast} + c_{2} p_{2}^{\ast})(c_{1} p_{1} + c_{2} p_{2}) d\tau}
\]

(3)

\[
\langle \varepsilon \rangle = \frac{\int c_{1}^{2} p_{1}^{\ast} \hat{H} p_{1} d\tau + \int c_{2}^{2} p_{2}^{\ast} \hat{H} p_{2} d\tau + \int c_{1} c_{2} p_{1}^{\ast} \hat{H} p_{2} d\tau + \int c_{2} c_{1} p_{2}^{\ast} \hat{H} p_{1} d\tau}{\int c_{1}^{2} p_{1}^{2} d\tau + \int c_{2}^{2} p_{2}^{2} d\tau + \int c_{1} c_{2} p_{1} p_{2} d\tau + \int c_{2} c_{1} p_{2} p_{1} d\tau}
\]

(4)

\[
\langle \varepsilon \rangle = \frac{c_{1}^{2} H_{11} + c_{2}^{2} H_{22} + c_{1} c_{2} H_{12} + c_{1} c_{2} H_{21}}{c_{1}^{2} + c_{2}^{2} + c_{1} c_{2} S_{12} + c_{1} c_{2} S_{21}}
\]

(5)

where \( H_{ij} = \int p_{i}^{\ast} \hat{H} p_{j} d\tau \)

\( S_{ij} = \int p_{i}^{\ast} p_{j} d\tau \)

(6)

(7)

The coefficients \( c_{1} \) and \( c_{2} \) can be treated as parameters, and the energy can be minimized with respect to each parameter. The resultant equations, (8) and (9) are known as secular equations.
\[
\frac{\partial \langle \varepsilon \rangle}{\partial c_1} = 0 = (H_{11} - \langle \varepsilon \rangle S_{11})c_1 + (H_{12} - \langle \varepsilon \rangle S_{12})c_2 \\
\frac{\partial \langle \varepsilon \rangle}{\partial c_2} = 0 = (H_{21} - \langle \varepsilon \rangle S_{21})c_1 + (H_{22} - \langle \varepsilon \rangle S_{22})c_2
\] (8) (9)

To solve this system of equations, the integrals $H_{ij}$ and $S_{ij}$ must be evaluated.

**Critical Thinking Questions**

3. Why are only two secular equations obtained for the $\pi$ system of ethylene?

4. If the trial function for a molecule contains four atomic orbitals, how many secular equations will be obtained?

5. Why is it desired to minimize the energy $\langle \varepsilon \rangle$ with respect to $c_1$ and $c_2$?

6. Why is $\frac{\partial \langle \varepsilon \rangle}{\partial c_i}$ set equal to zero?

7. For ethylene, do you expect $H_{11} = H_{22}$ and $S_{11} = S_{22}$? Explain your reasoning.
Model 2: Overlap of Two p Orbitals.

Case A

\[ \begin{array}{c}
    + \\
    - \\
    p_1 \\
    + \\
    - \\
    p_2 \\
\end{array} \]

Case B

\[ \begin{array}{c}
    + \\
    - \\
    p_1 \\
    + \\
    - \\
    p_2 \\
\end{array} \]

Case C

\[ \begin{array}{c}
    + \\
    - \\
    p_1 p_2 \\
    + \\
    - \\
    p_1 p_2 \\
\end{array} \]

Case D

\[ \begin{array}{c}
    + \\
    - \\
    p_1 \\
    p_2 \text{ superimposed} \\
\end{array} \]

Critical Thinking Questions

8. Which case in Model 2 has:
   
   (a) the most overlap between the two atomic orbitals, \( p_1 \) and \( p_2 \)?

   (b) the least overlap between the two atomic orbitals, \( p_1 \) and \( p_2 \)?

9. Predict which case in Model 2 is most likely the best description for the \( \pi \)-system of the ethylene molecule.
Model 3: Overlap of p Orbitals.

Assume that the orbitals \( p_1 \) and \( p_2 \) are real functions, and that they represent \( p \) orbitals on C atoms in ethylene.

Let \( p_1(y_d) \) represent the value of the function \( p_1 \) at the point \( y_d \).

![Diagram of p orbitals with points labeled](image)

**Critical Thinking Questions**

10. For each case, indicate whether the value of the \( p \) orbital in Model 3 is positive, negative, or zero: \( p_1(y_d) \); \( p_1(y_e) \); \( p_1(y_f) \); \( p_2(y_d) \); \( p_2(y_e) \); \( p_2(y_f) \)

11. Rank the following in terms of their relative magnitude and explain your reasoning: \( p_1(y_d) \); \( p_1(y_e) \); \( p_1(y_f) \)

12. Which has a greater magnitude: \( p_1(y_e) \) or \( p_2(y_e) \)? Explain your reasoning.
13. For each case, indicate whether the value is positive, negative, or zero, and then rank them in order of increasing magnitude:

\[ p_1(y_d) \cdot p_2(y_d); p_1(y_c) \cdot p_2(y_c); p_1(y_i) \cdot p_2(y_i) \]

14. Indicate the point \( y_g \) on the vertical line in Model 3 where the product \( p_1(y_g) \cdot p_2(y_g) \) is a minimum. What is the value of the product at this point?

15. Explain why the integral \( S_{12} \) cannot be negative for ethylene.

16. Explain, in words, why \( \int_{\text{all space}}^* p_1 \cdot p_2 \, d\tau \) for Case A in Model 2 is one.

17. Explain, in words, why \( \int_{\text{all space}}^* p_1 \cdot p_2 \, d\tau \) for Case D in Model 2 is essentially zero.

18. Rank the values of \( S_{12} \) in increasing order for Cases A, B, C, and D in Model 2.

**Information**

The integral \( \int_{\text{all space}}^* p_1 \cdot p_2 \, d\tau \) is called an *overlap integral*, \( S_{12} \), because its magnitude is the fraction of overlap for the orbitals on carbon atoms 1 and 2. The overlap integral has a value between zero (the orbitals are infinitely apart) and one (complete overlap).
Model 4: The Assumptions of HMO.

- \( S_{ij} = 0 \) when \( i \neq j \) (that is, all overlap integrals equal zero)
- \( S_{ii} = 1 \) (that is, all atomic orbitals are normalized)
- \( H_{ij} = \beta \) = the exchange integral when \( i \) and \( j \) are adjacent atoms

The exchange integral has no true classical analogy or interpretation. Examination of equation (6) reveals that this integral looks like an energy term that has the electron being shared by two different nuclei. When the two atoms are adjacent, we assume that the value of \( H_{ij} \) is sufficiently large that it cannot be ignored. We do not know the value of the exchange integral (at the moment). Later, we will determine the value of \( \beta \) from experimental evidence.

- \( H_{ij} = 0 \) when \( i \) and \( j \) are not adjacent atoms

When the two atoms are not adjacent, we assume that the value of \( H_{ij} \) is sufficiently small that it can be set to zero.

- \( H_{ii} = \alpha \) = the Coulomb integral

Examination of equation (6) reveals that when \( i = j \) this integral is an energy term corresponding to the electron being associated with one nucleus. We do not know the value of the Coulomb integral (at the moment). Generally, the Coulomb integral is viewed as the negative of the first \( IE \) of the isolated atom under consideration; for example, the first ionization energy of carbon is 1.09 MJ/mole and \( \alpha = -1.09 \) MJ/mole.

Both \( \alpha \) and \( \beta \) have energy values that are negative.

Critical Thinking Questions

19. Use the assumptions of HMO to rewrite equations (8) and (9). Show that the result is:

\[
0 = (\alpha - \varepsilon)c_1 + \beta c_2 \quad (10)
\]

\[
0 = \beta c_1 + (\alpha - \varepsilon)c_2 \quad (11)
\]

where \( \varepsilon = \langle \varepsilon \rangle \)

These equations are also called the secular equations.
20. Solve these equations by the "brute force" technique. That is, solve for $c_1$ (in terms of $\alpha$, $\beta$, $\epsilon$, and $c_2$) with equation (10). Use this value in equation (11) to solve for $<\mathcal{E}>$. [Hint: you will obtain two values for $<\mathcal{E}>$.]

21. Solve these equations by a "more elegant" technique. That is, solve for $<\mathcal{E}>$ by setting the determinant of the coefficients of the $c_i$ values in equation (10) and (11) equal to zero. You should obtain the same values for $<\mathcal{E}>$.

$$\begin{vmatrix}
(\alpha - \epsilon) & \beta \\
\beta & (\alpha - \epsilon)
\end{vmatrix} = 0$$
Model 5: The Energy Levels of the $\pi$-bond of Ethylene.

There are two electrons in the $\pi$-bond of ethylene.

$\begin{align*}
E & \uparrow \\
\alpha & \quad \alpha - \beta \\
\downarrow & \quad \alpha + \beta \\
\text{Case A} & \\
\downarrow & \quad \alpha - \beta \\
\downarrow & \quad \alpha + \beta \\
\text{Case B}
\end{align*}$

Critical Thinking Questions

22. Why is the energy level $\alpha + \beta$ at a lower energy than $\alpha - \beta$? [Hint: what is the sign of $\alpha$? Of $\beta$?]

23. Which case (A or B) in Model 5 would be called the ground state? The excited state?

24. How much energy is required to move the electron from the ground state to the excited state (in terms of $\beta$)?

Exercise

2. The electronic transition from the ground to excited state in ethylene occurs at 165 nm. Calculate a value for $\beta$ (in kJ/mole) based on the absorption in ethylene.
Information

The coefficients $c_1$ and $c_2$ are determined by using the normalization and orthogonality requirements of the wave functions. (Here we assume $\Psi$ is real for simplicity.)

First, solve for the general relationship between $c_1$ and $c_2$.

$$\Psi = c_1 p_1 + c_2 p_2$$

$$\int \Psi^2 d\tau = 1 = \int (c_1 p_1 + c_2 p_2) (c_1 p_1 + c_2 p_2) d\tau$$

$$1 = \int c_1^2 p_1^2 d\tau + \int c_2^2 p_2^2 d\tau + \int c_1 c_2 p_1 p_2 d\tau + \int c_1 c_2 p_2 p_1 d\tau$$

$$1 = c_1^2 + c_2^2 + c_1 c_2 S_{12} + c_1 c_2 S_{21} = c_1^2 + c_2^2$$

$$1 = c_1^2 + c_2^2$$  \hspace{1cm} (13)

Next, solve for the coefficients of the wave function associated with $\langle \epsilon \rangle = \alpha + \beta$. Either one of the secular equations can be used—(10) or (11). Here, equation (10) is used.

$$0 = (\alpha - \epsilon)c_1 + \beta c_2 = (\alpha - \alpha - \beta)c_1 + \beta c_2$$

$$\beta c_1 = \beta c_2$$

$$c_1 = c_2$$  \hspace{1cm} (14)

Combination of equations (13) and (14) yields:

$$c_1 = \frac{1}{\sqrt{2}} = c_2$$

Thus,

$$\epsilon_\pi = \alpha + \beta, \quad \Psi_\pi = \frac{1}{\sqrt{2}} p_1 + \frac{1}{\sqrt{2}} p_2$$  \hspace{1cm} (15)

Similarly, if $\epsilon = \alpha - \beta$ (higher energy state), then $c_1 = -c_2$:

$$\epsilon_{\pi^*} = \alpha - \beta, \quad \Psi_{\pi^*} = \frac{1}{\sqrt{2}} p_1 - \frac{1}{\sqrt{2}} p_2$$  \hspace{1cm} (16)
Model 6: The Energy Levels and Orbitals of the $\pi$-bond of Ethylene.

\[ \begin{align*}
\alpha - \beta & \quad \alpha + \beta \\
& \quad \pi \\
& \quad \pi^* \\
\end{align*} \]

Critical Thinking Questions

25. For the $\pi$ orbital, examine the wave function, equation (15), and the diagram in Model 6. Why are the two positive signs found on the same side of the molecular plane in Model 6?

26. For the $\pi^*$ orbital, examine the wave function, equation (16), and the diagram in Model 6. Why are the two positive signs found on the opposite sides of the molecular plane in Model 6?
27. Point B is equidistant from the two carbon nuclei. Suppose that $p_1$ has a value of $4.2 \times 10^{-6}$ pm$^{-3/2}$ at point B.

   a) What is the value of $\Psi_{\pi^*}$ at point B?

   b) What is the value of $\Psi_{\pi^*}$ at any point equidistant from the two nuclei?

28. How many nodes are there in $\Psi_{\pi}$? In $\Psi_{\pi^*}$? What is the relationship between the number of nodes and the energy of the mo?

**Exercises**

3. Show that $\Psi_{\pi^*}$ is normalized.

4. Show that the wave functions for the $\pi$ orbital and the $\pi^*$ orbital are orthogonal.
Conjugated π systems
(Is delocalization a good thing?)

The basic concepts of HMO theory were developed in the consideration of ethylene: the Linear Combination of Atomic Orbitals (LCAO); secular equations; the Coulomb integral; the exchange integral; the overlap integral. Now, we turn our attention to more complicated molecules, conjugated π systems.
Model 1: 1,3-butadiene.

\[
\begin{align*}
&H \quad C_1 \quad C_2 \quad C_3 \quad C_4 \quad H \\
&H - C_1 = C_2 = C_3 = C_4 = H
\end{align*}
\]

The trial function uses these four atomic orbitals.

\[
\Psi_{\text{trial}} = c_1 p_1 + c_2 p_2 + c_3 p_3 + c_4 p_4
\]  \hspace{1cm} (1)

As a result, there are four coefficients in the trial function. The trial function must be minimized with respect to each of the four coefficients.

\[
\frac{\partial \langle \varepsilon \rangle}{\partial c_1} = 0 = (H_{11} - \langle \varepsilon \rangle S_{11})c_1 + (H_{12} - \langle \varepsilon \rangle S_{12})c_2 + (H_{13} - \langle \varepsilon \rangle S_{13})c_3 + (H_{14} - \langle \varepsilon \rangle S_{14})c_4
\]

\[
\frac{\partial \langle \varepsilon \rangle}{\partial c_2} = 0 = (H_{21} - \langle \varepsilon \rangle S_{21})c_1 + (H_{22} - \langle \varepsilon \rangle S_{22})c_2 + (H_{23} - \langle \varepsilon \rangle S_{23})c_3 + (H_{24} - \langle \varepsilon \rangle S_{24})c_4
\]

\[
\frac{\partial \langle \varepsilon \rangle}{\partial c_3} = 0 = (H_{31} - \langle \varepsilon \rangle S_{31})c_1 + (H_{32} - \langle \varepsilon \rangle S_{32})c_2 + (H_{33} - \langle \varepsilon \rangle S_{33})c_3 + (H_{34} - \langle \varepsilon \rangle S_{34})c_4
\]

\[
\frac{\partial \langle \varepsilon \rangle}{\partial c_4} = 0 = (H_{41} - \langle \varepsilon \rangle S_{41})c_1 + (H_{42} - \langle \varepsilon \rangle S_{42})c_2 + (H_{43} - \langle \varepsilon \rangle S_{43})c_3 + (H_{44} - \langle \varepsilon \rangle S_{44})c_4
\]
Four secular equations are generated.

\[
\begin{align*}
0 &= (\alpha - \varepsilon) c_1 + \beta c_2 + 0 + 0 \\
0 &= \beta c_1 + (\alpha - \varepsilon) c_2 + \beta c_3 + 0 \\
0 &= 0 + \beta c_2 + (\alpha - \varepsilon) c_3 + \beta c_4 \\
0 &= 0 + 0 + \beta c_3 + (\alpha - \varepsilon) c_4
\end{align*}
\]

There are four solutions for the energy.

\[
\begin{align*}
\varepsilon_1 &= \alpha + 1.6180 \beta \\
\varepsilon_2 &= \alpha + 0.6180 \beta \\
\varepsilon_3 &= \alpha - 0.6180 \beta \\
\varepsilon_4 &= \alpha - 1.6180 \beta
\end{align*}
\]

Four wave functions are generated.

\[
\begin{align*}
\Psi_1 &= 0.3717\, p_1 + 0.6015\, p_2 + 0.6015\, p_3 + 0.3717\, p_4 \\
\Psi_2 &= 0.6015\, p_1 + 0.3717\, p_2 - 0.3717\, p_3 - 0.6015\, p_4 \\
\Psi_3 &= 0.6015\, p_1 - 0.3717\, p_2 - 0.3717\, p_3 + 0.6015\, p_4 \\
\Psi_4 &= 0.3717\, p_1 - 0.6015\, p_2 + 0.6015\, p_3 - 0.3717\, p_4
\end{align*}
\]

There is said to be a conservation of orbitals. The number of molecular orbitals generated is equal to the number of atomic orbitals used in the trial function.

A sketch of \(\Psi_1\) is shown below.
Critical Thinking Questions

1. Which energy level, $\epsilon_1$, is the lowest energy level?

2. Which orbital, $\Psi_1$, is represented below. Explain.

3. In CTQ 2, why is the $p$ orbital on carbon 1 depicted larger than the $p$ orbital on carbon 2?

4. If an electron is placed into $\Psi_2$, is the electron more likely to be found on carbon atom 1 or carbon atom 2? Explain.

5. The magnitude of the coefficients on carbon atoms 1 and 4 have the same value in any one molecular orbital, $\Psi_1$. Why must this be the case?

6. $\Psi_1$ does not have any nodes (other than the node in the molecular plane). How many nodes does $\Psi_2$ have? $\Psi_3$? $\Psi_4$?

7. What is the apparent relationship between the number of nodes of the orbital and the energy level of the orbital?
8. For \( \Psi_1 \), there appears to be bonding over all four carbon atoms. For \( \Psi_2 \), there appears to be bonding carbon atoms 1 and 2, bonding between carbon atoms 3 and 4, and a node between carbon atoms 2 and 3. What type of bonding or nodes seem to be evident between the carbon atoms when an electron is described by \( \Psi_4 \)?

**Exercises**

1. How many atomic orbitals should be used in the trial function for the \( \pi \) system of benzene? How many molecular orbitals would be generated?

2. How many atomic orbitals should be used in the trial function for the \( \pi \) system of naphthalene? How many molecular orbitals would be generated?

**Model 2: MO Diagram of the \( \pi \) System of 1,3-butadiene.**

\[
\begin{align*}
\Psi_4 & \quad -1.6180 \beta \\
\Psi_3 & \quad -0.6180 \beta \\
\Psi_2 & \quad 0.6180 \beta \\
\Psi_1 & \quad 1.6180 \beta
\end{align*}
\]

**Critical Thinking Questions**

9. What is the energy separation between \( \Psi_1 \) and \( \Psi_2 \)? \( \Psi_2 \) and \( \Psi_3 \)? \( \Psi_3 \) and \( \Psi_4 \)?

10. How many electrons are found in the \( \pi \) system of 1,3-butadiene?

11. The electron configuration of the ground state of 1,3-butadiene can be written as \( \Psi_1^2 \Psi_2^2 \). Write the electron configuration of the lowest-energy excited state of 1,3-butadiene?
Model 3: $\pi$-electron Charge Densities and $\pi$-electron Charges.

The square of a coefficient of an atomic orbital is taken as the fraction of an electron found near that atom (by each electron in an occupied molecular orbital). That is, for one electron in the molecular orbital

$$\Psi_2 = 0.6015 \, p_1 + 0.3717 \, p_2 - 0.3717 \, p_3 - 0.6015 \, p_4$$

0.3618 of the electron is found at atom 1, 0.1382 at atom 2, and so on. Thus, the $\pi$-electron charge density (a misnomer), $q$, at atom $r$ is given by

$$q_r = \sum_i n_i \, (c_{ir})^2$$  \hspace{1cm} (2)$$

where $n_i$ is the number of electrons in the $i$th molecular orbital, $c_{ir}$ is the coefficient of atom $r$ in the $i$th molecular orbital, and the sum is over all molecular orbitals containing one or more electrons.

The $\pi$-electron charge (also a misnomer) on atom $r$ is taken as the number of electrons that an atom contributes to the $\pi$ system minus the charge density, $q_r$. For example, if a carbon atom contributes one electron to the $\pi$ system and has a $\pi$-electron charge density of 1.023, then the charge on the carbon atom is $-0.023$. On the other hand, if a pyrrole-like nitrogen contributes two electrons to the $\pi$ system and has a $\pi$-electron charge density of 1.988, then the charge on the nitrogen atom is +0.012.

Critical Thinking Questions

12. Give a rationale for taking the square of a coefficient of an atomic orbital as the fraction of an electron found near that atom (by each electron in an occupied molecular orbital)?

13. What is the sum of the squares of all the coefficients for $\Psi_2$? Explain why this makes sense.

14. Why does the number of electrons in the orbital, $n_i$, appear in equation (2)?
Exercises

3. Refer to Model 2 and CTQ 11. Calculate the π-electron charge density on atom 1, \( q_1 \), for the ground state of 1,3-butadiene. Calculate the π-electron charge density on atom 2, \( q_2 \). Without doing any calculations, what is the π-electron charge density on atom 3? On atom 4?

4. According to your energy level diagram for 1,3-butadiene, what is the \( \Delta \varepsilon \) for the lowest energy electronic transition (in terms of \( \beta \))? Use your value of \( \beta \), calculated in CA 14, Exercise 2 to determine the wavelength of this transition. The experimental value for 1,3-butadiene is 217 nm. How well does your calculated value compare to the experimental value?

5. The lowest energy resonance structure and numbering system for imidazole is shown below:

![Diagram of imidazole]

a. Draw two resonance structures for imidazole that show that the lone-pair electrons on N1 (the pyrrole-type nitrogen) are contributors to the π system. (These same resonance structures will show that the lone-pair electrons on N3 (the pyridine-type nitrogen) are not contributors to the π system.)

b. Give the total number of electrons in the π-system of imidazole. How many electrons are contributed by N1? By C2? By N3? By C4? By C5?

c. Give the total number of p-orbitals in the π-system of imidazole. How many orbitals are contributed by N1? By C2? By N3? By C4? By C5?

d. The HMO energy levels for the π-system of imidazole are:
\[
\begin{align*}
\varepsilon_1 & = \alpha + 2.3737 \beta \\
\varepsilon_2 & = \alpha + 1.3785 \beta \\
\varepsilon_3 & = \alpha + 0.6736 \beta \\
\varepsilon_4 & = \alpha - 0.9586 \beta \\
\varepsilon_5 & = \alpha - 1.4672 \beta
\end{align*}
\]

Make a π-system energy level diagram for imidazole and place the correct number of electrons into the diagram.
e. The HMO wave functions for the π-system of imidazole are:

\[ \Psi_1 = 0.6911 \, p_1 + 0.3907 \, p_2 + 0.3746 \, p_3 + 0.3112 \, p_4 + 0.3640 \, p_5 \]

\[ \Psi_2 = 0.6055 \, p_1 - 0.1168 \, p_2 - 0.6454 \, p_3 - 0.4502 \, p_4 + 0.0248 \, p_5 \]

\[ \Psi_3 = 0.0826 \, p_1 + 0.5354 \, p_2 + 0.2945 \, p_3 - 0.4842 \, p_4 - 0.6207 \, p_5 \]

\[ \Psi_4 = 0.3835 \, p_1 - 0.6700 \, p_2 + 0.3354 \, p_3 + 0.1808 \, p_4 - 0.5087 \, p_5 \]

\[ \Psi_5 = 0.0428 \, p_1 + 0.3133 \, p_2 - 0.4939 \, p_3 + 0.6583 \, p_4 - 0.4720 \, p_5 \]

A sketch of the top-view of \( \Psi_1 \) is shown below:

[Sketch of the top-view of \( \Psi_1 \)]

Make a sketch of the top view of the other four molecular orbitals.

f. If an electron is placed into \( \Psi_1 \), which atom "has" most of the electron? Which atom "has" least of the electron?

g. Calculate the π-electron charge density on atom 2 for the ground state configuration.

h. Calculate the π-electron charge on atom 2 for the ground state configuration.
Model 4: \( \pi \)-electron Bond Orders.

Bonding takes place when there is a significant sharing of electron density between two atoms. For an occupied orbital, the electron sharing is large when the wave function is large between the adjacent atoms. Thus, the bond order between adjacent atoms is considered to be large when the coefficients on the adjacent atoms are large and have the same sign. The \( \pi \)-electron bond order is another defined quantity. For adjacent atoms \( r \) and \( s \), the bond order is given by

\[
P_{ts} = \sum_{i} n_{i} (c_{ir} c_{is})
\]  

(3)

where \( c_{ir} \) and \( c_{is} \) are the coefficients of atom \( r \) and \( s \), respectively, in the \( i \)th molecular orbital, and the sum is taken over all orbitals.

Critical Thinking Questions

15. Suppose the coefficients for the \( p \) orbitals on two adjacent atoms are 0.50 and 0.01, respectively. Suppose the coefficients for the \( p \) orbitals between a second set of adjacent atoms is 0.25 and 0.26. Give a rationale for taking the products of the coefficients rather than the sum of the coefficients as a measure of the bond strength.

16. Suppose the coefficients for the \( p \) orbitals on two adjacent atoms are -0.25 and -0.26. Give a rationale for taking the products of the coefficients rather than the sum of the coefficients as a measure of the bond strength.

17. Suppose the coefficients for the \( p \) orbitals on two adjacent atoms are 0.25 and -0.26. Does this represent bonding between the two atoms, or will there be a node between the two atoms?
18. Why does the number of electrons in the orbital, $n_i$, appear in equation 3?

Exercises

6. For the ground state of 1,3-butadiene, calculate the $\pi$-electron bond order $p_{12}$. Calculate the $\pi$-electron bond order $p_{23}$. Without doing any calculations, give the $\pi$-electron bond order $p_{34}$.

7. What is the sum of the number of $\pi$ bonds in the lowest energy resonance structure of 1,3-butadiene? What is the sum of the number of $\pi$ bonds in the HMO description of 1,3-butadiene? That is, what is the sum of $p_{12}, p_{23}, p_{34}$? Explain why the amount of $\pi$-bonding is greater using HMO than with the lowest energy resonance structure.

8. Calculate the $\pi$-electron bond order between atom 2 and atom 3 in imidazole.