CHEM20212
Computational Chemistry II:
Fundamentals of electronic structure theory

4 Hückel theory

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Course Overview

1 Electronic structure of atoms • Introduction • Hydrogenic atoms • Multi-electron atoms • Ground *vs.* excited states	**4 Hückel theory** • Constructing a Hückel matrix • Molecular orbitals • Benzene anion • Electrophilic and nucleophilic attack
2 Electronic structure of molecules • Molecular orbitals • Molecular electronic structure • Energy hierarchy	**5 Spin Hamiltonians** • A "how-to" guide • Matrix elements • Example: $S = 1/2$ • Example: $S = 1$
3 Matrix mechanics • Vector (Hilbert) spaces • Bra-ket notation • Operators and expectation values • Matrix diagonalisation	**6 Workshop**

Intended learning objectives

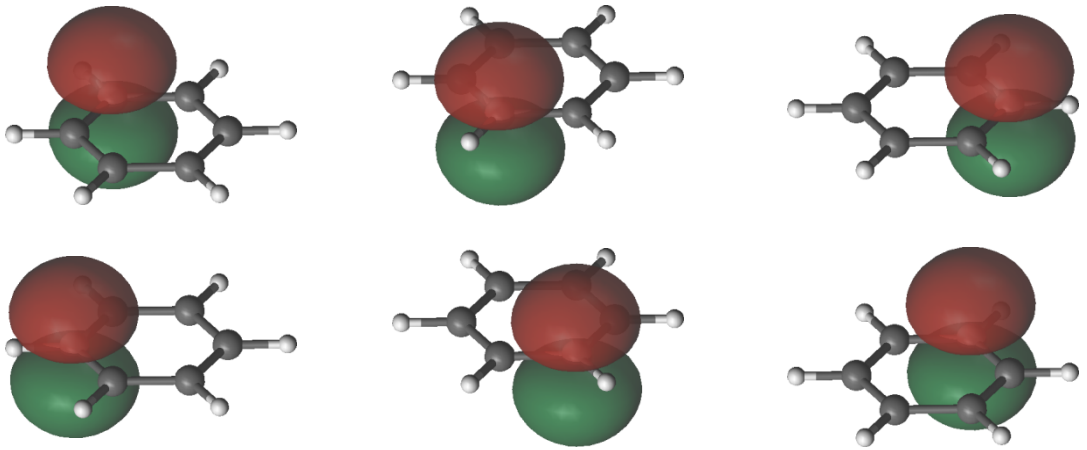
1. Construct approximate wave functions for single and multi-electron atoms
2. Explain the energy hierarchy of multi-electron atoms
3. Differentiate the concepts of ground and excited electronic states, including spin and orbital states
4. Mathematically expand and visualise the spatial wave functions of atoms and simple molecules as a linear combination of MOs and basis functions
5. Mathematically describe the connection between matrix diagonalisation and solution to the Schrödinger equation
6. Construct a Hückel Hamiltonian matrix
7. Employ Bra-Ket notation to evaluate the matrix elements of a simple spin Hamiltonian

Hückel theory

- Hückel theory is a simple and elegant way for calculating the ***spatial*** MOs of planar π electron systems

- It completely neglects the σ electrons, but does provide useful results for certain applications!

- Our basis set is formed from the p_z orbitals on each carbon atom perpendicular to the plane of the molecule
  - *e.g.* for benzene



Constructing a Hückel matrix

- For benzene, we have six basis functions (the p_z orbitals on each carbon atom)
  - Let's ***assume*** that they are an orthogonal, normalised basis (of course, this is not true!)

- Therefore, our Hamiltonian has a dimension equal to the number of conjugated carbon atoms
  - The basis vectors are:

$$\left|p_{z_1}\right\rangle \equiv \begin{bmatrix}1\\0\\0\\0\\0\\0\end{bmatrix}, \left|p_{z_2}\right\rangle \equiv \begin{bmatrix}0\\1\\0\\0\\0\\0\end{bmatrix}, \left|p_{z_3}\right\rangle \equiv \begin{bmatrix}0\\0\\1\\0\\0\\0\end{bmatrix}, \left|p_{z_4}\right\rangle \equiv \begin{bmatrix}0\\0\\0\\1\\0\\0\end{bmatrix}, \left|p_{z_5}\right\rangle \equiv \begin{bmatrix}0\\0\\0\\0\\1\\0\end{bmatrix}, \left|p_{z_6}\right\rangle \equiv \begin{bmatrix}0\\0\\0\\0\\0\\1\end{bmatrix}$$

Constructing a Hückel matrix

- To solve for the wavefunction, we need to determine the Hamiltonian matrix, and diagonalise it:

$$P^{-1}\overline{\overline{\hat{H}}}P = D$$

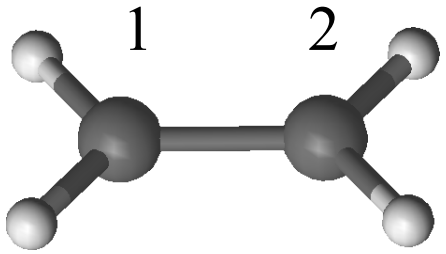
- The matrix elements are defined as:

$\langle p_{z_i}|\hat{H}|p_{z_i}\rangle = \alpha$
$\langle p_{z_i}|\hat{H}|p_{z_k}\rangle = \beta$ if atoms i and k are bonded
$\langle p_{z_i}|\hat{H}|p_{z_k}\rangle = 0$ for all other elements

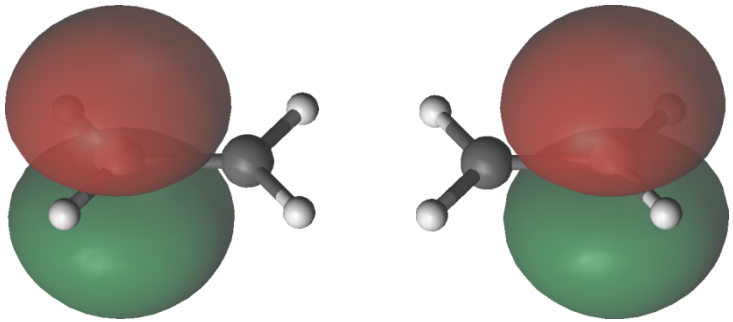
  - Where ***both α and β are less than zero***

Constructing a Hückel matrix

- Let's start with ethene (C_2H_4):
  - Atom labelling:



  - Basis orbitals:



  - Basis vectors:

$$\left|p_{z_1}\right\rangle \equiv \begin{bmatrix}1\\0\end{bmatrix}, \left|p_{z_2}\right\rangle \equiv \begin{bmatrix}0\\1\end{bmatrix}$$

  - Hückel Hamiltonian matrix:

$$\hat{\hat{H}} = \begin{matrix}1\\2\end{matrix} \begin{bmatrix}\langle p_{z_1}|\hat{H}|p_{z_1}\rangle & \langle p_{z_1}|\hat{H}|p_{z_2}\rangle\\ \langle p_{z_2}|\hat{H}|p_{z_1}\rangle & \langle p_{z_2}|\hat{H}|p_{z_2}\rangle\end{bmatrix}^{\begin{matrix}1 & 2\end{matrix}} = \begin{matrix}1\\2\end{matrix} \begin{bmatrix}\alpha & \beta\\ \beta & \alpha\end{bmatrix}$$

Molecular orbitals

- Diagonalising $\hat{\hat{\hat{H}}}$ we get the two eigenvectors and eigenvalues:
  - Should be familiar from last lecture!

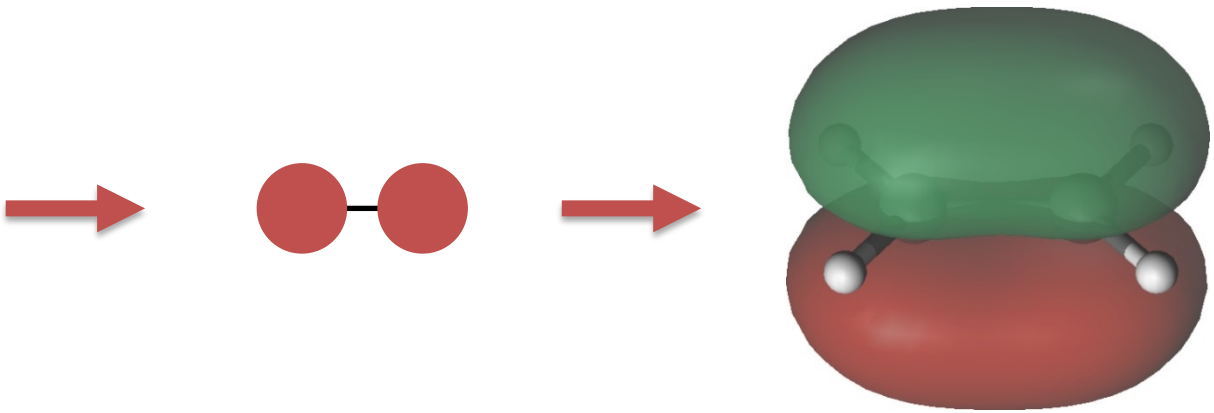
$$E_1 = \alpha + \beta \qquad E_2 = \alpha - \beta$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix} \qquad |\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\end{bmatrix}$$

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_1 = \alpha + \beta$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}$$

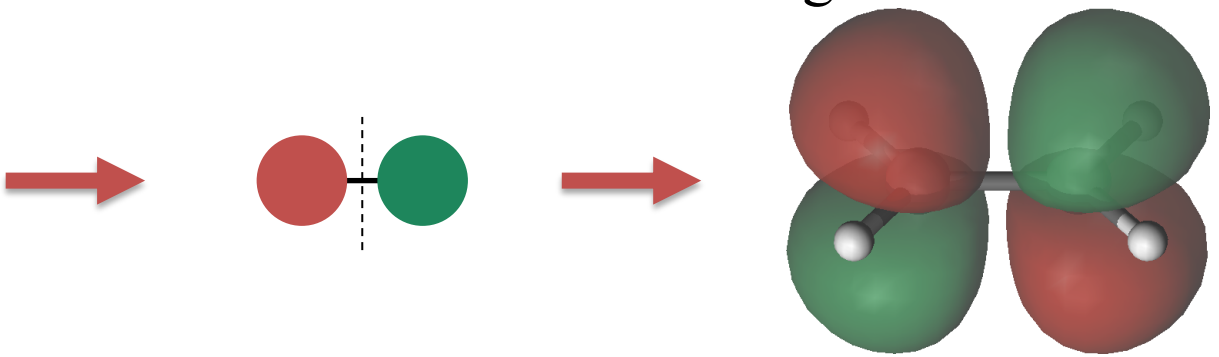


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

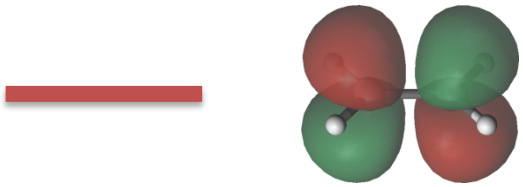
$$E_2 = \alpha - \beta$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

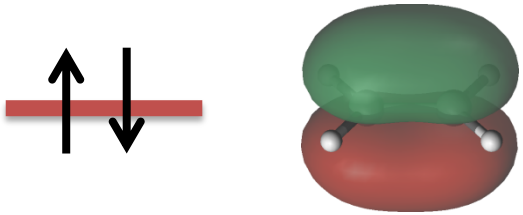


- Therefore, the π electronic structure for ethene is (remember, α and β are negative):

$$E_2 = \alpha - \beta$$

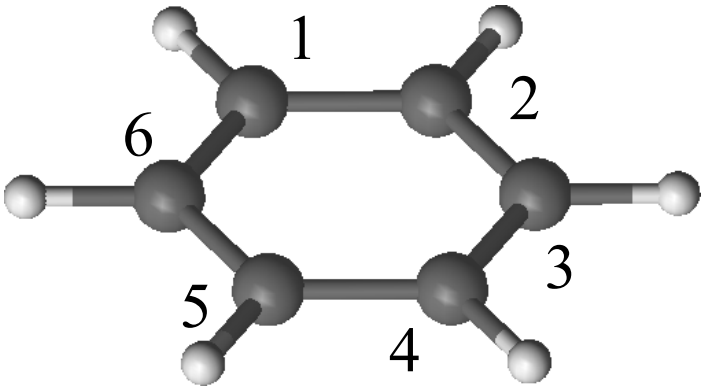


$$E_1 = \alpha + \beta$$



Constructing a Hückel matrix

- What does the Hückel Hamiltonian look like for benzene?



$$\hat{\hat{H}} = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{array}{c} \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{bmatrix} \end{array}$$

Molecular orbitals

- Diagonalising $\hat{\hat{\hat{H}}}$ we find the six eigenvectors and eigenvalues:

$$E_1 = \alpha + 2\beta \qquad |\psi_1\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix}1\\1\\1\\1\\1\\1\end{bmatrix}$$

$$E_2 = \alpha + \beta \qquad |\psi_2\rangle = \frac{1}{2\sqrt{3}}\begin{bmatrix}1\\2\\1\\-1\\-2\\-1\end{bmatrix}$$

$$E_3 = \alpha + \beta \qquad |\psi_3\rangle = \frac{1}{2}\begin{bmatrix}1\\0\\-1\\-1\\0\\1\end{bmatrix}$$

$$E_4 = \alpha - \beta \qquad |\psi_4\rangle = \frac{1}{2}\begin{bmatrix}1\\0\\-1\\1\\0\\-1\end{bmatrix}$$

$$E_5 = \alpha - \beta \qquad |\psi_5\rangle = \frac{1}{2\sqrt{3}}\begin{bmatrix}1\\-2\\1\\1\\-2\\1\end{bmatrix}$$

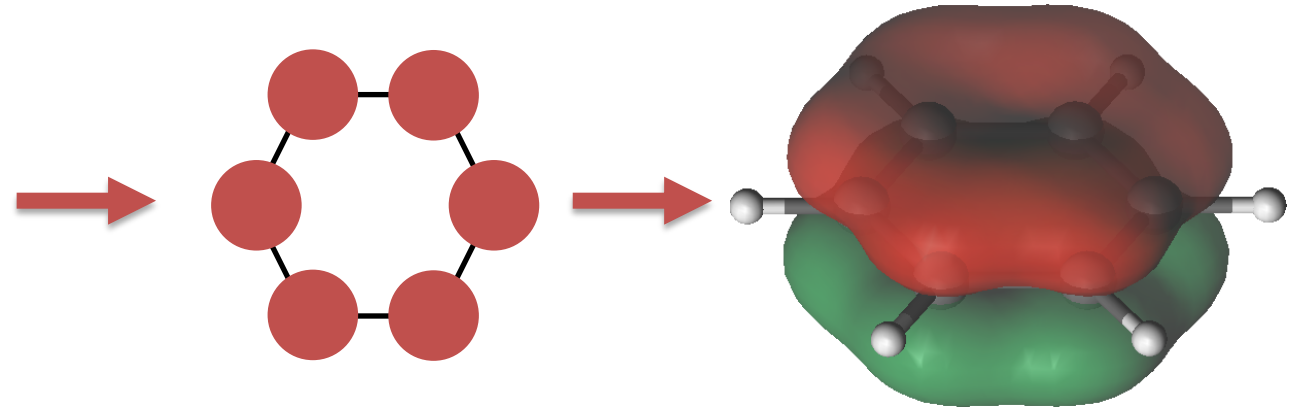
$$E_6 = \alpha - 2\beta \qquad |\psi_6\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix}1\\-1\\1\\-1\\1\\-1\end{bmatrix}$$

Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_1 = \alpha + 2\beta$$

$$|\psi_1\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix}1\\1\\1\\1\\1\\1\end{bmatrix}$$

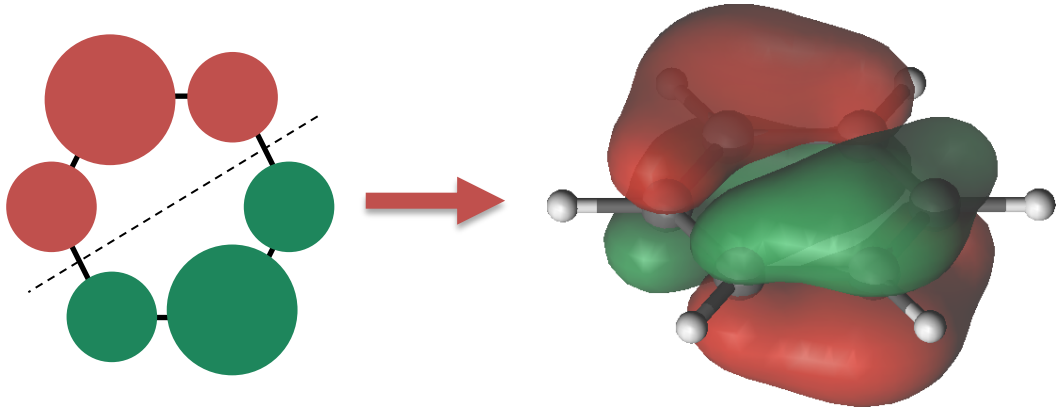


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_2 = \alpha + \beta$$

$$|\psi_2\rangle = \frac{1}{2\sqrt{3}}\begin{bmatrix} 1 \\ 2 \\ 1 \\ -1 \\ -2 \\ -1 \end{bmatrix}$$

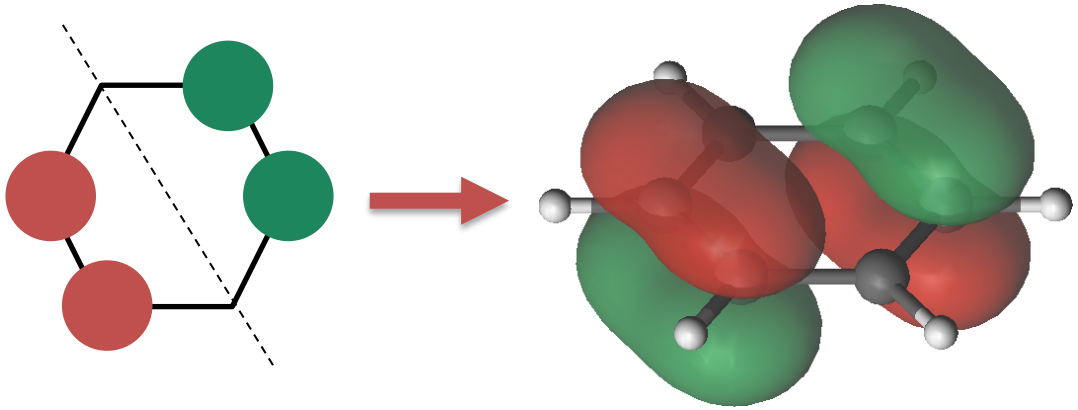


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_3 = \alpha + \beta$$

$$|\psi_3\rangle = \frac{1}{2}\begin{bmatrix} 1 \\ 0 \\ -1 \\ -1 \\ 0 \\ 1 \end{bmatrix}$$

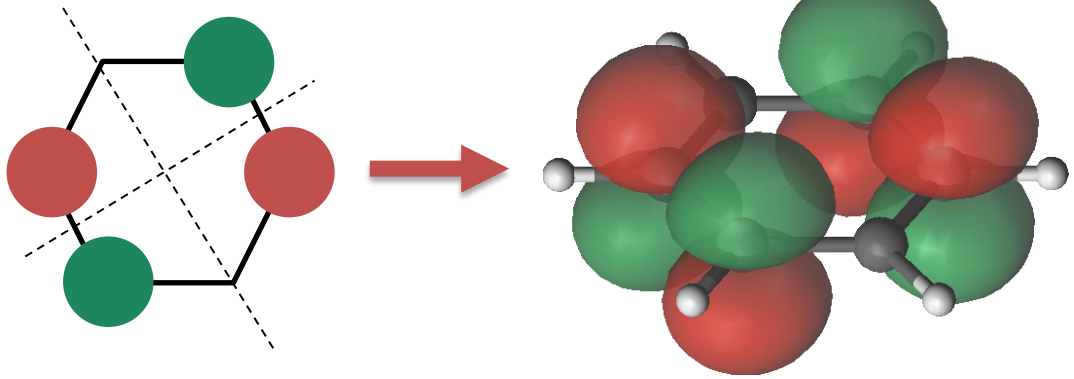


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_4 = \alpha - \beta$$

$$|\psi_4\rangle = \frac{1}{2}\begin{bmatrix} 1 \\ 0 \\ -1 \\ 1 \\ 0 \\ -1 \end{bmatrix}$$

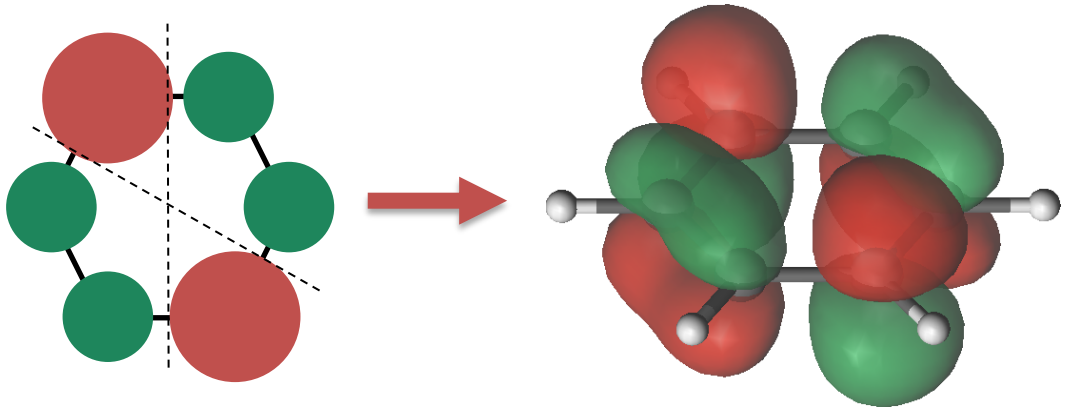


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

$$E_5 = \alpha - \beta$$

$$|\psi_5\rangle = \frac{1}{2\sqrt{3}}\begin{bmatrix} 1 \\ -2 \\ 1 \\ 1 \\ -2 \\ 1 \end{bmatrix}$$

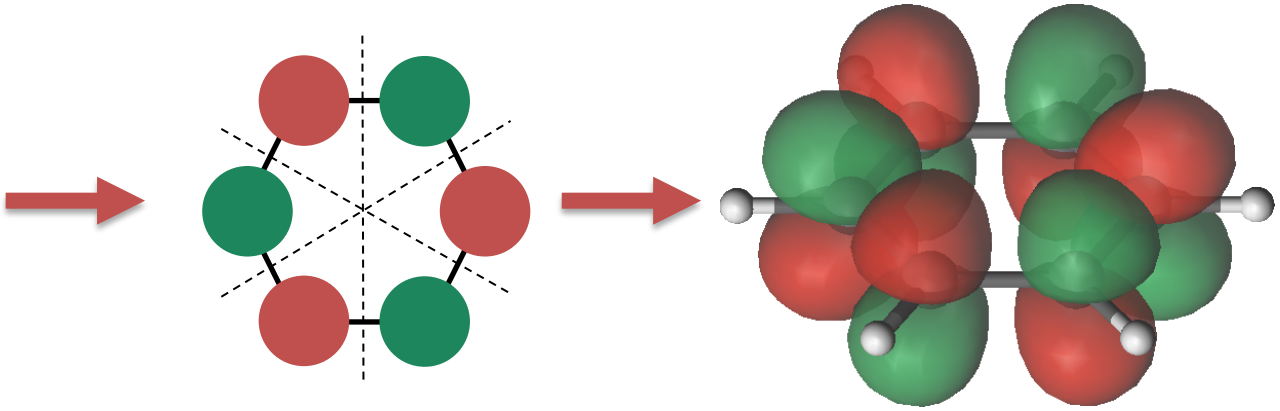


Molecular orbitals

- What do the MOs look like?
  - Scale size of basis function by relative magnitude of coefficient and add or subtract based on sign

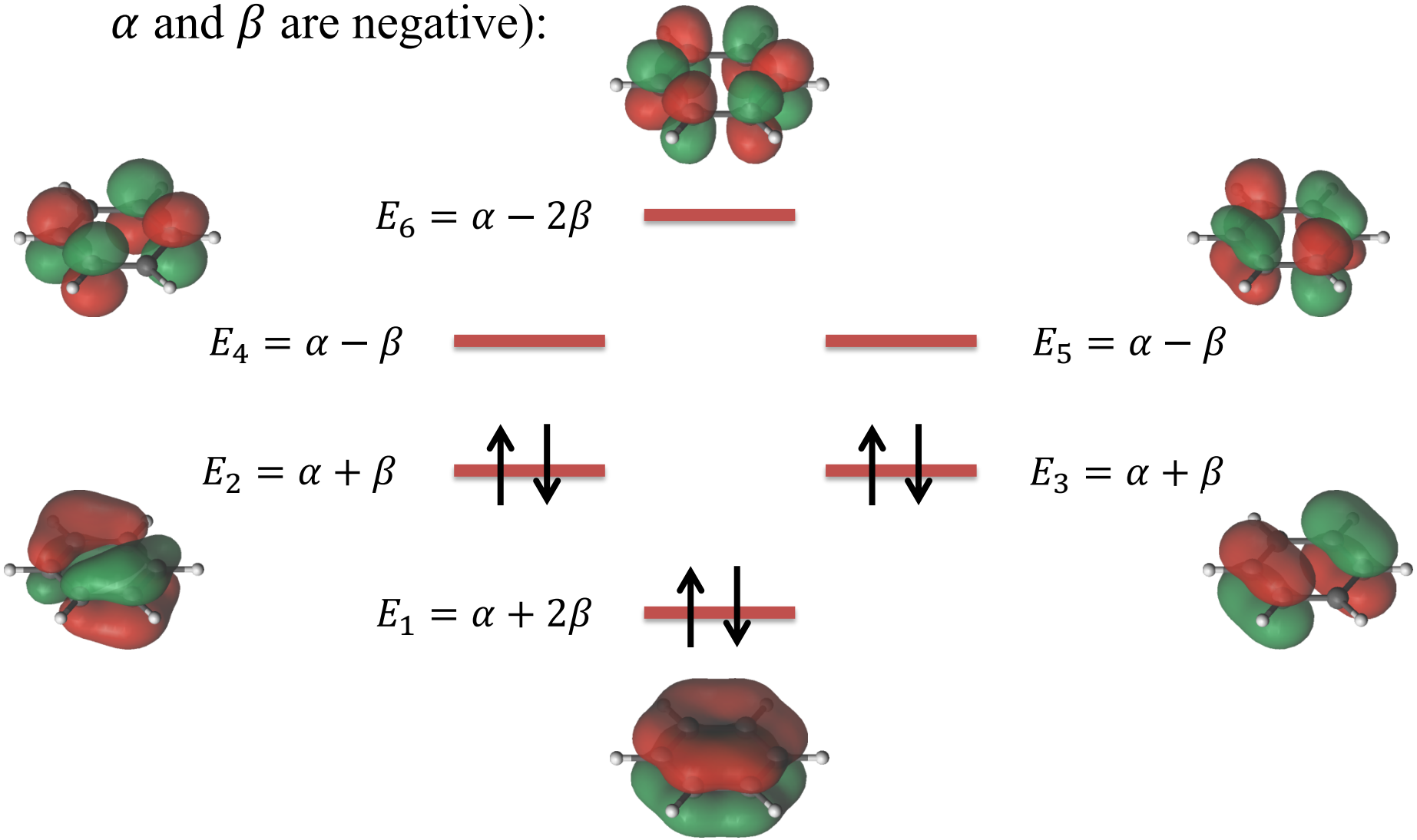
$$E_6 = \alpha - 2\beta$$

$$|\psi_6\rangle = \frac{1}{\sqrt{6}}\begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \\ 1 \\ -1 \end{bmatrix}$$



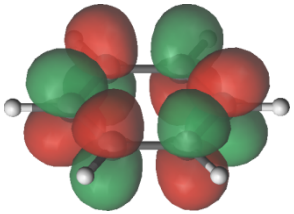
Molecular orbitals

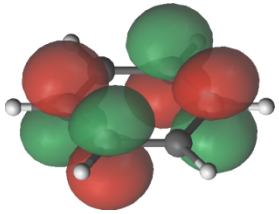
- Therefore, the π electronic structure for benzene is (remember, α and β are negative):



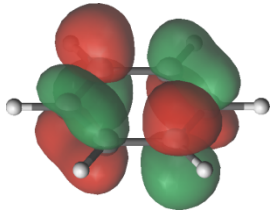
Benzene anion

- If we reduce benzene, where does the electron go?

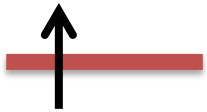




$E_6 = \alpha - 2\beta$

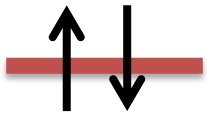


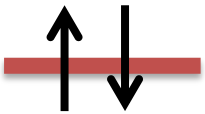
$E_4 = \alpha - \beta$



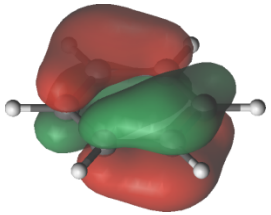
$E_5 = \alpha - \beta$

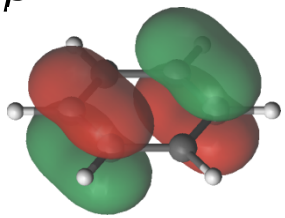
$E_2 = \alpha + \beta$



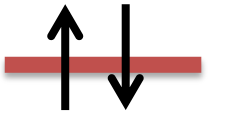


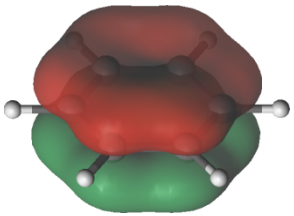
$E_3 = \alpha + \beta$





$E_1 = \alpha + 2\beta$





Benzene anion

- Which carbon atoms carry the unpaired spin density?
- Probability of wavefunction (electron density):

$$\int_r \overline{\Psi[\vec{r}]}\Psi[\vec{r}]d\vec{r} \equiv \langle\Psi|\Psi\rangle$$

  - Ignoring paired electrons, only have one electron: no need to construct a Slater determinant
  - BUT! Two need to consider both configurations:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\psi_4\rangle + |\psi_5\rangle)$$

Benzene anion

- Which carbon atoms carry the unpaired spin density?

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\psi_4\rangle + |\psi_5\rangle)$$

  - Expanding:

$$\langle\Psi|\Psi\rangle = \frac{1}{2}(\langle\psi_4| + \langle\psi_5|)(|\psi_4\rangle + |\psi_5\rangle)$$

$$= \frac{1}{2}(\langle\psi_4|\psi_4\rangle + \langle\psi_4|\psi_5\rangle + \langle\psi_5|\psi_4\rangle + \langle\psi_5|\psi_5\rangle)$$

$$= \frac{1}{2}(\langle\psi_4|\psi_4\rangle + \langle\psi_5|\psi_5\rangle) = \frac{1}{2}\left(\sum_i^{basis}\left[{C_{\psi_4,i}}^2 + {C_{\psi_5,i}}^2\right]\right)$$

  - Notice spin density is sum over atomic contributions!

$$\langle\Psi|\Psi\rangle = \sum_i^{basis} \rho_i \; ; \; \rho_i = \frac{1}{2}\left({C_{\psi_4,i}}^2 + {C_{\psi_5,i}}^2\right)$$

Benzene anion

- The density localised on each carbon atom is given by the component corresponding to each p_z basis function:

$$\rho_i = \frac{1}{2}\left(C_{\psi_{4,i}}{}^2 + C_{\psi_{5,i}}{}^2\right) \qquad |\psi_4\rangle = \frac{1}{2}\begin{bmatrix}1\\0\\-1\\1\\0\\-1\end{bmatrix} \qquad |\psi_5\rangle = \frac{1}{2\sqrt{3}}\begin{bmatrix}1\\-2\\1\\1\\-2\\1\end{bmatrix}$$

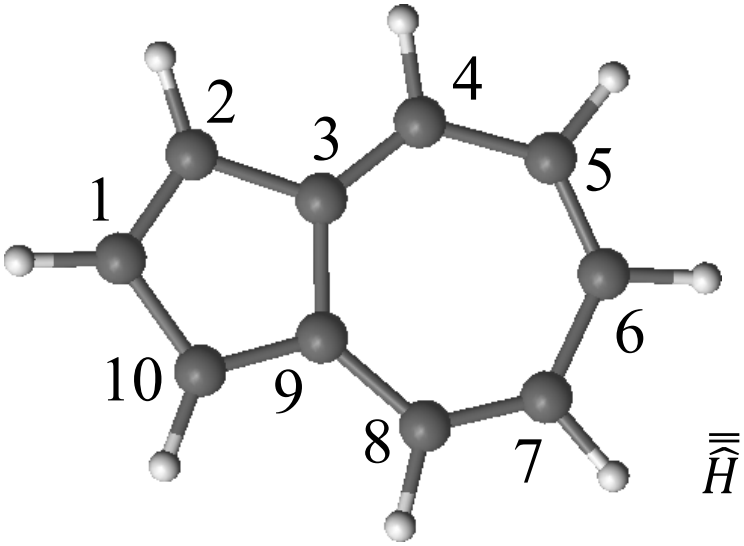
$$\rho_1 = \frac{1}{2}\left(\frac{1}{4} + \frac{1}{12}\right) = \frac{1}{6} \qquad \rho_3 = \frac{1}{2}\left(\frac{1}{4} + \frac{1}{12}\right) = \frac{1}{6} \qquad \rho_5 = \frac{1}{2}\left(0 + \frac{4}{12}\right) = \frac{1}{6}$$

$$\rho_2 = \frac{1}{2}\left(0 + \frac{4}{12}\right) = \frac{1}{6} \qquad \rho_4 = \frac{1}{2}\left(\frac{1}{4} + \frac{1}{12}\right) = \frac{1}{6} \qquad \rho_6 = \frac{1}{2}\left(\frac{1}{4} + \frac{1}{12}\right) = \frac{1}{6}$$

- ***Equal spin density on all carbon atoms!***

Electrophilic and nucleophilic attack

- We can use the Hückel method to calculate which atoms are likely to be subject to electrophilic and nucleophilic attack
  - Consider azulene (fused 5- and 7-member rings):



$$\hat{\hat{\hat{H}}} = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \end{array} \begin{array}{c} \begin{array}{cccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \end{array} \\ \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & \beta & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & \beta & 0 & 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha \end{bmatrix} \end{array}$$

Electrophilic and nucleophilic attack

$E_1 = \alpha + 2.31\beta$

$$|\psi_1\rangle = \begin{bmatrix} 0.280 \\ 0.323 \\ 0.467 \\ 0.289 \\ 0.200 \\ 0.173 \\ 0.200 \\ 0.289 \\ 0.467 \\ 0.323 \end{bmatrix}$$

$E_2 = \alpha + 1.65\beta$

$$|\psi_2\rangle = \begin{bmatrix} 0.324 \\ 0.268 \\ 0.118 \\ -0.191 \\ -0.433 \\ -0.520 \\ -0.433 \\ -0.191 \\ 0.118 \\ 0.268 \end{bmatrix}$$

$E_3 = \alpha + 1.36\beta$

$$|\psi_3\rangle = \begin{bmatrix} 0 \\ -0.221 \\ -0.299 \\ -0.484 \\ -0.357 \\ 0 \\ 0.357 \\ 0.484 \\ 0.299 \\ 0.221 \end{bmatrix}$$

$E_4 = \alpha + 0.89\beta$

$$|\psi_4\rangle = \begin{bmatrix} 0.580 \\ 0.259 \\ -0.354 \\ -0.219 \\ 0.160 \\ 0.360 \\ 0.160 \\ -0.219 \\ -0.354 \\ 0.259 \end{bmatrix}$$

$E_5 = \alpha + 0.48\beta$

$$|\psi_5\rangle = \begin{bmatrix} 0 \\ -0.540 \\ -0.259 \\ 0.160 \\ 0.335 \\ 0 \\ -0.335 \\ -0.160 \\ 0.259 \\ 0.540 \end{bmatrix}$$

$E_6 = \alpha - 0.40\beta$

$$|\psi_6\rangle = \begin{bmatrix} -0.316 \\ 0.063 \\ 0.290 \\ -0.470 \\ -0.102 \\ 0.510 \\ -0.102 \\ -0.470 \\ 0.290 \\ 0.063 \end{bmatrix}$$

$E_7 = \alpha - 0.74\beta$

$$|\psi_7\rangle = \begin{bmatrix} 0 \\ -0.299 \\ 0.221 \\ 0.357 \\ -0.484 \\ 0 \\ 0.484 \\ -0.357 \\ -0.221 \\ 0.299 \end{bmatrix}$$

$E_8 = \alpha - 1.58\beta$

$$|\psi_8\rangle = \begin{bmatrix} -0.550 \\ 0.436 \\ -0.136 \\ -0.084 \\ 0.270 \\ -0.342 \\ 0.270 \\ -0.084 \\ -0.136 \\ 0.436 \end{bmatrix}$$

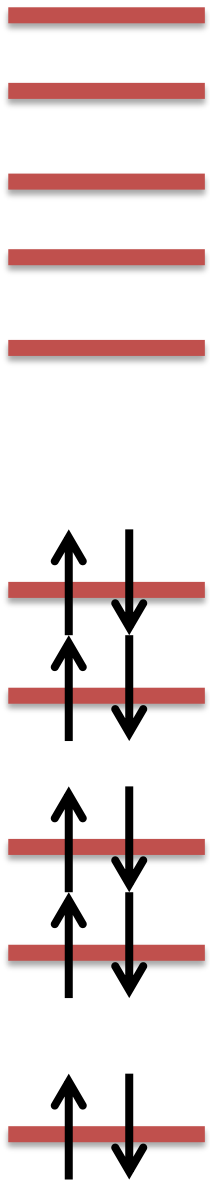
$E_9 = \alpha - 1.87\beta$

$$|\psi_9\rangle = \begin{bmatrix} -0.267 \\ 0.250 \\ -0.200 \\ 0.323 \\ -0.405 \\ 0.433 \\ -0.405 \\ 0.323 \\ -0.200 \\ 0.250 \end{bmatrix}$$

$E_{10} = \alpha - 2.10\beta$

$$|\psi_{10}\rangle = \begin{bmatrix} 0 \\ -0.259 \\ 0.540 \\ -0.335 \\ 0.160 \\ 0 \\ -0.160 \\ 0.335 \\ -0.540 \\ 0.259 \end{bmatrix}$$

Electrophilic and nucleophilic attack



- Total electron density:

$$\rho_i = \sum_{k=1}^{MOs} occ_k C_{\psi_{k,i}}{}^2$$

$$\rho_i = 2\sum_{k=1}^{5} C_{\psi_{k,i}}{}^2$$

- Sum of the squares of the MO coefficients associated with each carbon atom, multiplied by occupation number

Electrophilic and nucleophilic attack

$E_1 = \alpha + 2.31\beta$ $E_2 = \alpha + 1.65\beta$ $E_3 = \alpha + 1.36\beta$ $E_4 = \alpha + 0.89\beta$ $E_5 = \alpha + 0.48\beta$

$$|\psi_1\rangle = \begin{bmatrix} \mathbf{0.280} \\ 0.323 \\ 0.467 \\ 0.289 \\ 0.200 \\ 0.173 \\ 0.200 \\ 0.289 \\ 0.467 \\ 0.323 \end{bmatrix} \quad |\psi_2\rangle = \begin{bmatrix} \mathbf{0.324} \\ 0.268 \\ 0.118 \\ -0.191 \\ -0.433 \\ -0.520 \\ -0.433 \\ -0.191 \\ 0.118 \\ 0.268 \end{bmatrix} \quad |\psi_3\rangle = \begin{bmatrix} \mathbf{0} \\ -0.221 \\ -0.299 \\ -0.484 \\ -0.357 \\ 0 \\ 0.357 \\ 0.484 \\ 0.299 \\ 0.221 \end{bmatrix} \quad |\psi_4\rangle = \begin{bmatrix} \mathbf{0.580} \\ 0.259 \\ -0.354 \\ -0.219 \\ 0.160 \\ 0.360 \\ 0.160 \\ -0.219 \\ -0.354 \\ 0.259 \end{bmatrix} \quad |\psi_5\rangle = \begin{bmatrix} \mathbf{0} \\ -0.540 \\ -0.259 \\ 0.160 \\ 0.335 \\ 0 \\ -0.335 \\ -0.160 \\ 0.259 \\ 0.540 \end{bmatrix}$$

$$\rho_1 = 2\sum_{k=1}^{5} {C_{k_{k,1}}}^2 = 2(0.280^2 + 0.324^2 + 0^2 + 0.580^2 + 0^2)$$

$$= 2(0.0784 + 0.1050 + 0.3364) = 2\times 0.5198 = 1.040$$

Electrophilic and nucleophilic attack

$E_1 = \alpha + 2.31\beta$ $E_2 = \alpha + 1.65\beta$ $E_3 = \alpha + 1.36\beta$ $E_4 = \alpha + 0.89\beta$ $E_5 = \alpha + 0.48\beta$

$$|\psi_1\rangle = \begin{bmatrix} 0.280 \\ 0.323 \\ 0.467 \\ \mathbf{0.289} \\ 0.200 \\ 0.173 \\ 0.200 \\ 0.289 \\ 0.467 \\ 0.323 \end{bmatrix} \quad |\psi_2\rangle = \begin{bmatrix} 0.324 \\ 0.268 \\ 0.118 \\ \mathbf{-0.191} \\ -0.433 \\ -0.520 \\ -0.433 \\ -0.191 \\ 0.118 \\ 0.268 \end{bmatrix} \quad |\psi_3\rangle = \begin{bmatrix} 0 \\ -0.221 \\ -0.299 \\ \mathbf{-0.484} \\ -0.357 \\ 0 \\ 0.357 \\ 0.484 \\ 0.299 \\ 0.221 \end{bmatrix} \quad |\psi_4\rangle = \begin{bmatrix} 0.580 \\ 0.259 \\ -0.354 \\ \mathbf{-0.219} \\ 0.160 \\ 0.360 \\ 0.160 \\ -0.219 \\ -0.354 \\ 0.259 \end{bmatrix} \quad |\psi_5\rangle = \begin{bmatrix} 0 \\ -0.540 \\ -0.259 \\ \mathbf{0.160} \\ 0.335 \\ 0 \\ -0.335 \\ -0.160 \\ 0.259 \\ 0.540 \end{bmatrix}$$

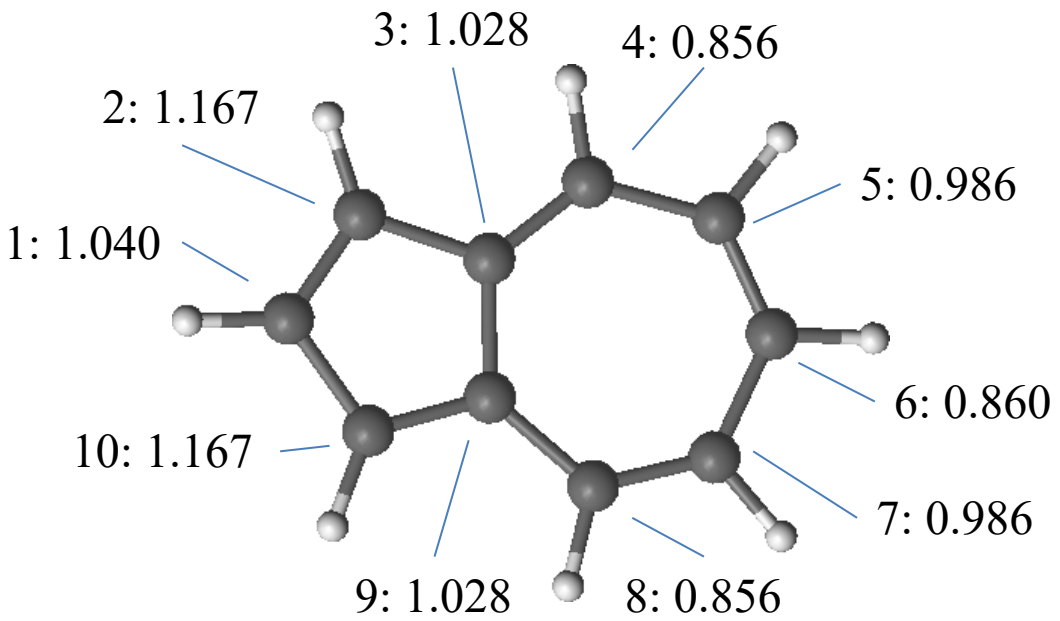
$$\rho_4 = 2\sum_{k=1}^{5} {C_{\psi_{k,4}}}^2 = 2(0.289^2 + 0.191^2 + 0.484^2 + 0.219^2 + 0.160^2)$$

$$= 2(0.0835 + 0.0365 + 0.2343 + 0.0480 + 0.0256)$$

$$= 2\times 0.4279 = 0.856$$

Electrophilic and nucleophilic attack

- We find:



  - Positions 2 and 10: electrophilic substitution
  - Positions 4 and 8: nucleophilic substitution
  - ***In agreement with experiment!***

FEED FORWARD: electron *vs.* spin density

- Electron density on atom i:

$$\rho_i = \sum_{k=1}^{MOs} occ_k C_{\psi_{k,i}}{}^2$$

  - occ_k is either 0, 1 or 2
  - $C_{\psi_{k,i}}$ is the coefficient for atom i in eigenvector k

- Spin density on atom i: same equation, but only care about unpaired electrons! Ignore orbitals with 2 or 0, occ_k is 1!
  - Non-degenerate SOMO: N degenerate SOMOs:

$$\rho_i = C_{\psi_{SOMO,i}}{}^2 \qquad \rho_i = \frac{1}{N} \sum_{k}^{SOMOs} C_{\psi_{k,i}}{}^2$$