

4. Molecules

March 15, 2018

Review: Molecules I

Every property of a molecule can be calculated using quantum mechanics.

$$H_{\text{mp}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}$$

Make some approximations.

$$H_{\text{red}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}.$$

$$H_{\text{red}}(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_N) = H_{\text{mo}}(\vec{r}_1) + H_{\text{mo}}(\vec{r}_2) + \dots + H_{\text{mo}}(\vec{r}_N).$$

$$\Psi_{\text{red}}(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_N) = |\psi_{\text{mo}}(\vec{r}_1)\psi_{\text{mo}}(\vec{r}_2) \dots \psi_{\text{mo}}(\vec{r}_N)\rangle.$$

Molecular orbital Hamiltonian:
$$H_{\text{mo}} = - \frac{\hbar^2}{2m_e} \nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}.$$

The exact solution to H_{red} can be constructed from the solutions to H_{mo} .

Review: Molecules II

$$H_{\text{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}.$$

The molecular orbitals are constructed using LCAO.

$$\psi_{\text{mo}}(\vec{r}) = \sum_a \sum_{ao} c_{ao,a} \phi_{ao}^{Z_a}(\vec{r} - \vec{r}_a).$$

Substitute into $H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}$, construct the Roothaan equations.

The many electron wavefunction is constructed as a Slater determinant.

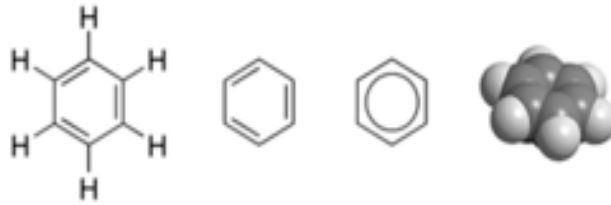
$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \approx |\psi_{\text{mo}1} \uparrow(\vec{r}_1), \psi_{\text{mo}2} \uparrow(\vec{r}_2), \dots, \psi_{\text{mo}N} \uparrow(\vec{r}_N)\rangle.$$

This is an exact solution to H_{red} and an approximate solution to H_{mp} .

The energy is calculated including the electron-electron interactions.

$$E = \frac{\langle \Psi | H_{\text{mp}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Benzene



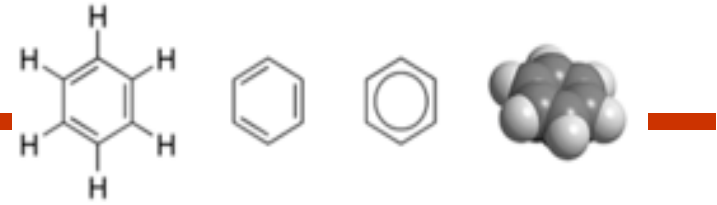
42 electrons

hydrogen 1s
carbon 1s, 2s, 2p

36 relevant atomic orbitals

$$\psi_{mo} = c_1 \phi_{1s}^{H1} + \dots + c_7 \phi_{1s}^{C1} + \dots + c_{13} \phi_{2s}^{C1} + \dots + c_{19} \phi_{2px}^{C1} + \dots + c_{25} \phi_{2py}^{C1} + \dots + c_{31} \phi_{2pz}^{C1} + \dots + c_{36} \phi_{2pz}^{C6}$$

Benzene



| | | | | | |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 | 0 |
| 0 | 1 | 0 | 0 | 0 | 0 |
| 0 | 0 | 1 | 0 | 0 | 0 |
| 0 | 0 | 0 | 1 | 0 | 0 |
| 0 | 0 | 0 | 0 | 1 | 0 |
| 0 | 0 | 0 | 0 | 0 | 1 |

↑
C 1s

0

H 1s, C 2s, 2p_x, 2p_y

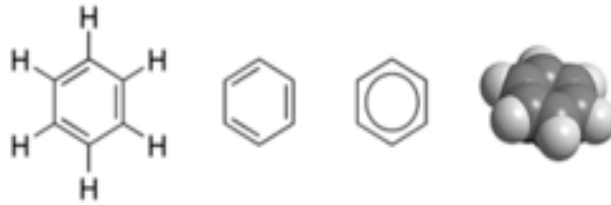
0

0

| | | | | | |
|----------|----------|----------|----------|----------|----------|
| 1 | S_{12} | 0 | 0 | 0 | S_{12} |
| S_{12} | 1 | S_{12} | 0 | 0 | 0 |
| 0 | S_{12} | 1 | S_{12} | 0 | 0 |
| 0 | 0 | S_{12} | 1 | S_{12} | 0 |
| 0 | 0 | 0 | S_{12} | 1 | S_{12} |
| S_{12} | 0 | 0 | 0 | S_{12} | 1 |

← C 2p_z

Benzene

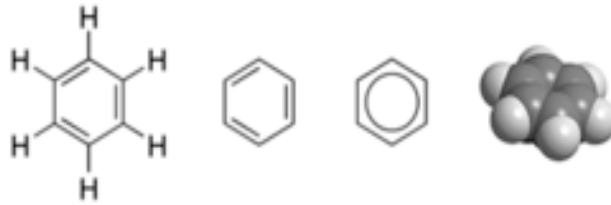


Assume the valence molecular orbital is

$$\Psi_{MO} = c_1\phi_{2p_z,1}^C + c_2\phi_{2p_z,2}^C + c_3\phi_{2p_z,3}^C + c_4\phi_{2p_z,4}^C + c_5\phi_{2p_z,5}^C + c_6\phi_{2p_z,6}^C$$

$$H\Psi_{MO} = E\Psi_{MO}$$

Benzene



$$\begin{bmatrix} H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\ 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\ 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\ 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & 0 & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & 0 & 0 & S_{12} \\ S_{12} & 1 & S_{12} & 0 & 0 & 0 \\ 0 & S_{12} & 1 & S_{12} & 0 & 0 \\ 0 & 0 & S_{12} & 1 & S_{12} & 0 \\ 0 & 0 & 0 & S_{12} & 1 & S_{12} \\ S_{12} & 0 & 0 & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} .$$

$$H_{ij} = \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_i) | H_{\text{mo}} | \phi_{2p_z}^C(\vec{r} - \vec{r}_j) \rangle \quad \text{and} \quad S_{ij} = \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_i) | \phi_{2p_z}^C(\vec{r} - \vec{r}_j) \rangle$$

Translation operator

$$T\vec{u} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_1 \end{bmatrix}$$

$$T^2\vec{u} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_1 \\ u_2 \end{bmatrix}$$

T and T² have the same eigenvectors

Translation operator

$$\mathbf{T}^N = \mathbf{I}$$

$$\mathbf{T}^N \vec{u} = \mathbf{I} \vec{u} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix}$$

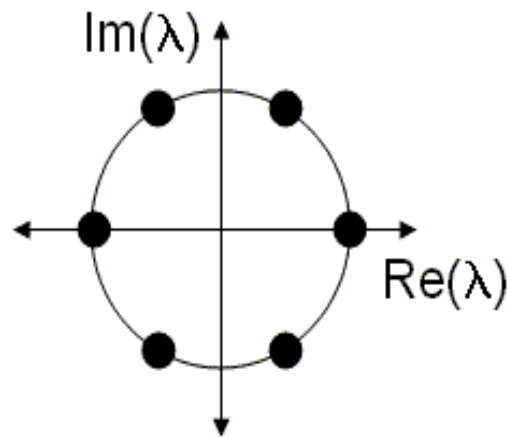
$$\mathbf{T}^{-1} \vec{u} = \mathbf{T}^{N-1} \vec{u} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix} u_6 \\ u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{bmatrix}.$$

Eigen values of the translation operator

$$T\vec{u} = \lambda\vec{u}$$

$$T^N\vec{u} = \lambda^N\vec{u} = \vec{u}$$

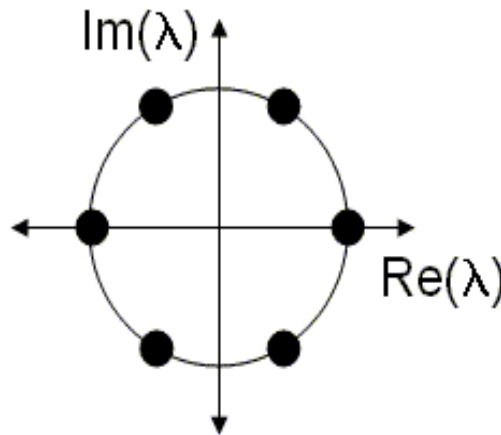
$$\lambda^N = 1$$



For each eigenvalue, solve $(T - \lambda I)\vec{u} = 0$ to determine the eigenvectors.

Eigen vectors of the translation operator

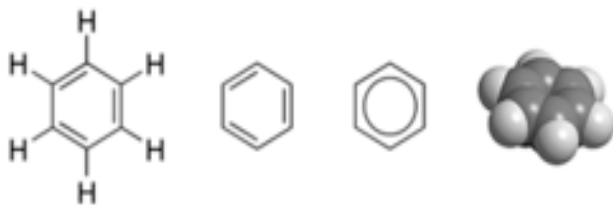
$$T = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$



$$\begin{bmatrix} 1 \\ e^{i\pi j/3} \\ e^{i2\pi j/3} \\ e^{i\pi j} \\ e^{-i2\pi j/3} \\ e^{-i\pi j/3} \end{bmatrix} \quad j = 1, \dots, 6$$

$$1, \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}; e^{i2\pi/6}, \begin{bmatrix} 1 \\ e^{i2\pi/6} \\ e^{i4\pi/6} \\ e^{i6\pi/6} \\ e^{i8\pi/6} \\ e^{i10\pi/6} \end{bmatrix}; e^{i4\pi/6}, \begin{bmatrix} 1 \\ e^{i4\pi/6} \\ e^{i8\pi/6} \\ e^{i12\pi/6} \\ e^{i16\pi/6} \\ e^{i20\pi/6} \end{bmatrix}; -1, \begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \\ 1 \\ -1 \end{bmatrix}; e^{i8\pi/6}, \begin{bmatrix} 1 \\ e^{i8\pi/6} \\ e^{i16\pi/6} \\ e^{i24\pi/6} \\ e^{i32\pi/6} \\ e^{i40\pi/6} \end{bmatrix}; e^{i10\pi/6}, \begin{bmatrix} 1 \\ e^{i10\pi/6} \\ e^{i20\pi/6} \\ e^{i30\pi/6} \\ e^{i40\pi/6} \\ e^{i50\pi/6} \end{bmatrix}$$

Benzene

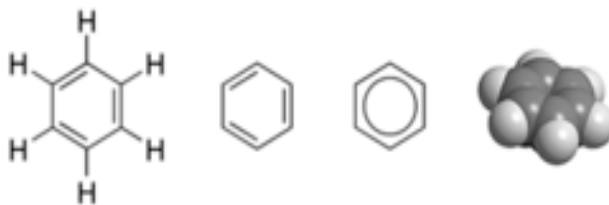


$$\begin{bmatrix} H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\ 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\ 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\ 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & 0 & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & 0 & 0 & S_{12} \\ S_{12} & 1 & S_{12} & 0 & 0 & 0 \\ 0 & S_{12} & 1 & S_{12} & 0 & 0 \\ 0 & 0 & S_{12} & 1 & S_{12} & 0 \\ 0 & 0 & 0 & S_{12} & 1 & S_{12} \\ S_{12} & 0 & 0 & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix}$$

$$H = H_{11}\mathbf{I} + H_{12}\mathbf{T} + H_{12}\mathbf{T}^{-1}$$

$$S = \mathbf{I} + S_{12}\mathbf{T} + S_{12}\mathbf{T}^{-1}$$

Benzene



$$\begin{bmatrix} H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\ 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\ 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\ 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & 0 & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} 1 \\ e^{i\pi j/3} \\ e^{i2\pi j/3} \\ e^{i\pi j} \\ e^{-i2\pi j/3} \\ e^{-i\pi j/3} \end{bmatrix} = H_{11} + H_{12} \left(e^{i\pi j/3} + e^{-i\pi j/3} \right) \begin{bmatrix} 1 \\ e^{i\pi j/3} \\ e^{i2\pi j/3} \\ e^{i\pi j} \\ e^{-i2\pi j/3} \\ e^{-i\pi j/3} \end{bmatrix}$$

$$e^{i\pi j/3} + e^{-i\pi j/3} = 2 \cos\left(\frac{\pi j}{3}\right)$$

$$j = 1, 2, \dots, N$$

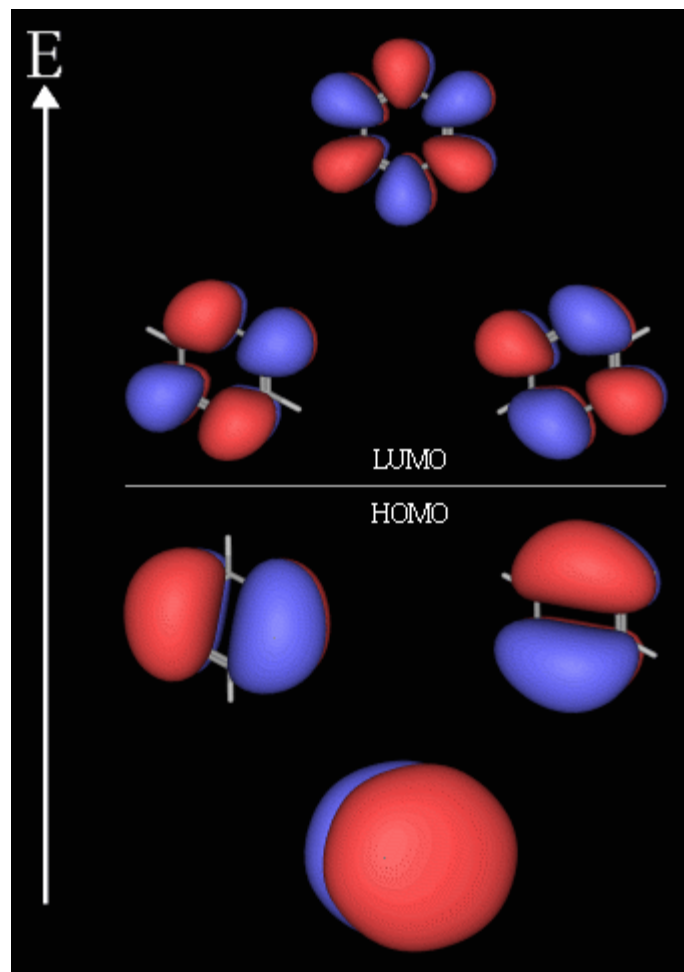
Benzene

$$\psi_j = \varphi_{2p_z1}^C + e^{i\pi j/3} \varphi_{2p_z2}^C + e^{i2\pi j/3} \varphi_{2p_z3}^C + e^{i\pi j} \varphi_{2p_z4}^C + e^{-i2\pi j/3} \varphi_{2p_z5}^C + e^{-i\pi j/3} \varphi_{2p_z6}^C$$

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = \begin{bmatrix} 1 \\ e^{i\pi j/3} \\ e^{i2\pi j/3} \\ e^{i\pi j} \\ e^{-i2\pi j/3} \\ e^{-i\pi j/3} \end{bmatrix}$$

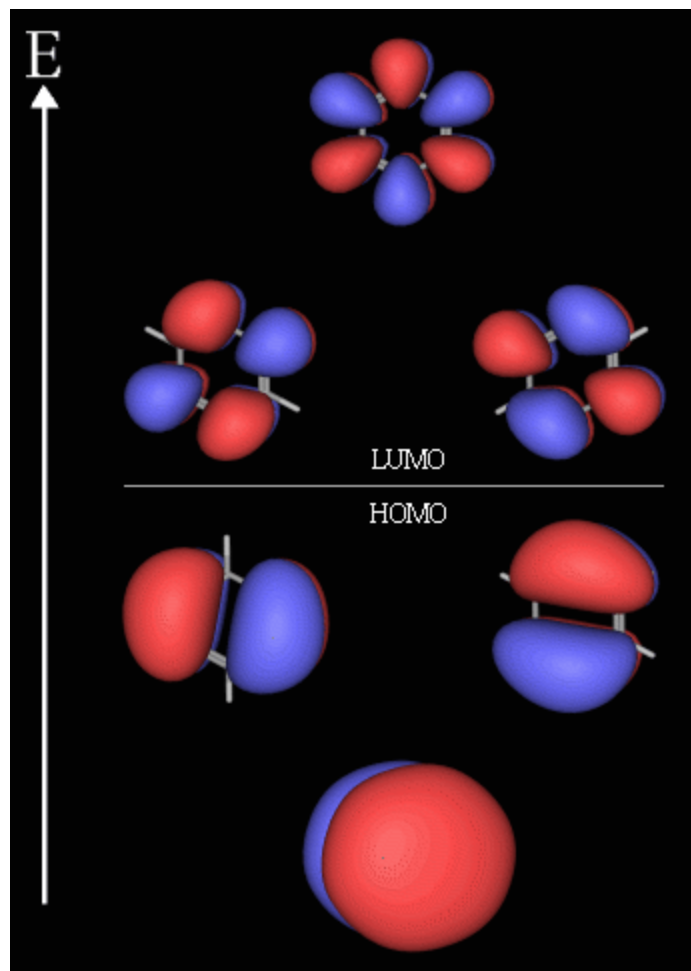
$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{\pi j}{3}\right)}{1 + 2S_{12} \cos\left(\frac{\pi j}{3}\right)}$$

$$j = 1, 2, \dots, 6.$$

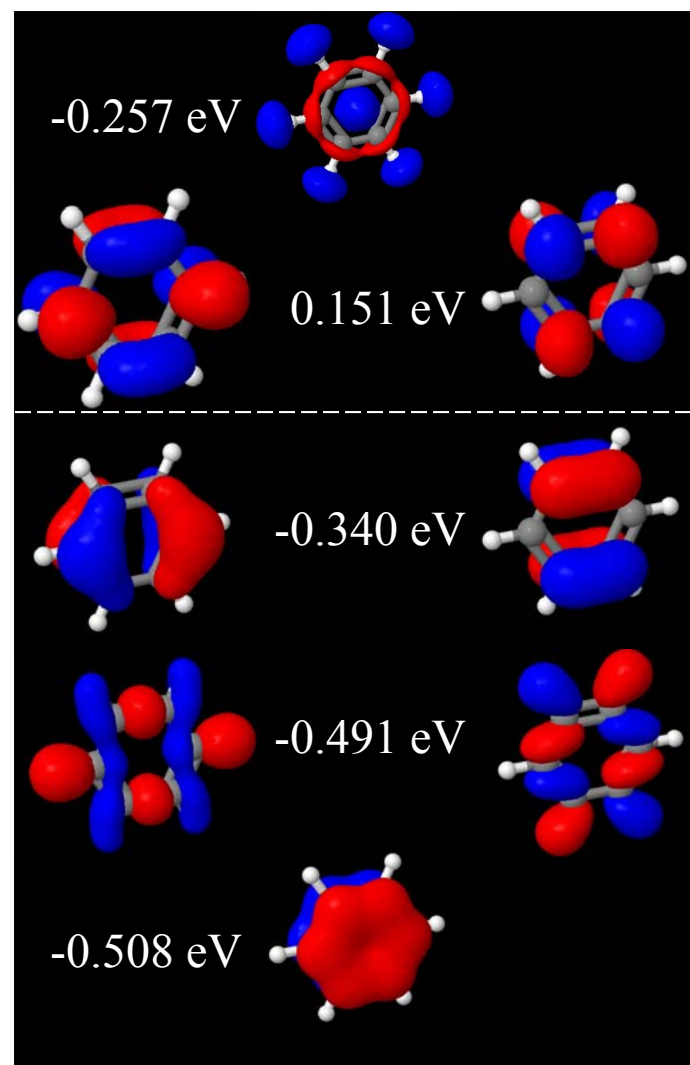


Molecular orbitals benzene

<http://www.chemcomp.com/journal/molorbbs.htm>



$$E_j = H_{11} + 2H_{12} \cos\left(\frac{\pi j}{3}\right) \quad j = 1, 2, \dots, 6$$



<http://www.stolaf.edu/people/hansonr/jmol/mo/>

Molecular orbitals of a conjugated ring

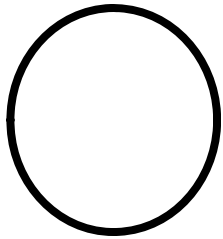
The Roothaan equations for a conjugated ring of N atoms have the form,

$$\begin{bmatrix} H_{11} & H_{12} & 0 & \cdots & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & & 0 \\ 0 & H_{12} & H_{11} & H_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & \cdots & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & \cdots & 0 & S_{12} \\ S_{12} & 1 & S_{12} & 0 & & 0 \\ 0 & S_{12} & 1 & S_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & S_{12} & 1 & S_{12} \\ S_{12} & 0 & \cdots & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix}.$$

$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{2\pi j}{N}\right)}{1 + 2S_{12} \cos\left(\frac{2\pi j}{N}\right)} \quad j = 1, 2, \dots, N.$$

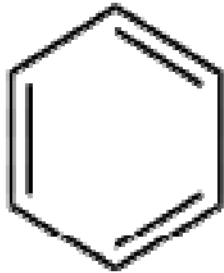
$$\psi_{\text{mo},j} = \frac{1}{\sqrt{N}} \sum_{n=1}^N \exp\left(\frac{i2\pi nj}{N}\right) \phi_{2pz}^C(\vec{r} - \vec{r}_n) \quad j = 1, 2, \dots, N.$$

Particles confined to a ring



$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\theta) = -\frac{\hbar^2}{2mR^2} \frac{\partial^2 \psi(\theta)}{\partial \theta^2} = E\psi(\theta)$$

$$\psi_n = \frac{e^{in\theta}}{\sqrt{2\pi}} \quad n = 0, \pm 1, \pm 2, \dots$$

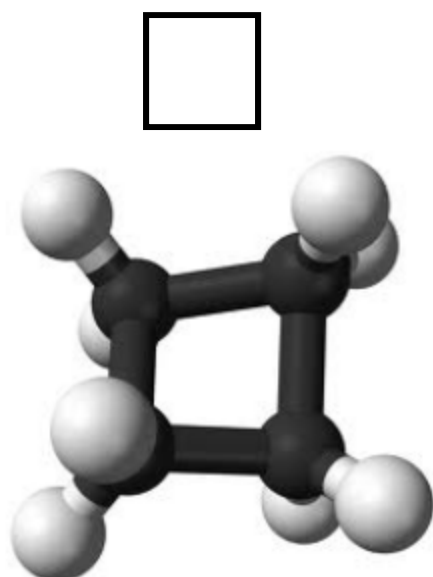


$$E_n = \frac{\hbar^2 n^2}{2mR^2}$$

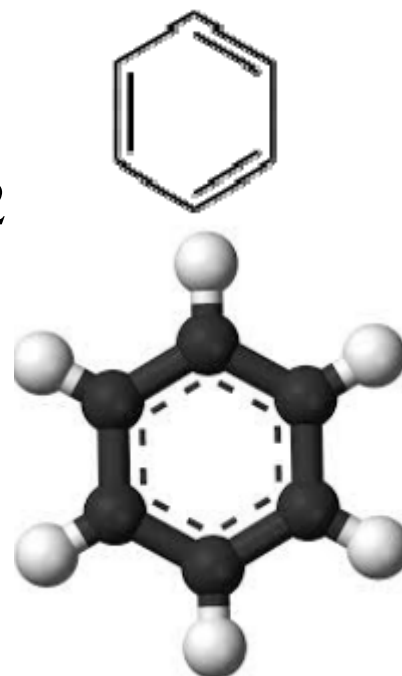
Aromatic molecules obey Hückel's $4n + 2$ rule
Molecules that don't obey the $4n+2$ rule are radicals

Particles confined to a ring

cyclobutane



benzene

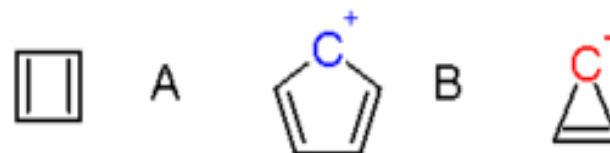


$$4n + 2$$

Antiaromaticity

From Wikipedia, the free encyclopedia

Antiaromatic molecules are cyclic systems containing alternating single and double bonds, where the pi electron energy of antiaromatic compounds is higher than that of its open-chain counterpart. Therefore antiaromatic compounds are unstable and highly reactive; often antiaromatic compounds distort themselves out of planarity to resolve this instability. Antiaromatic compounds usually fail Hückel's rule of aromaticity.



Radicals

Molecules are most stable with a closed shell configuration.

Ar

H₂O 10 electrons

NH₃

CH₄

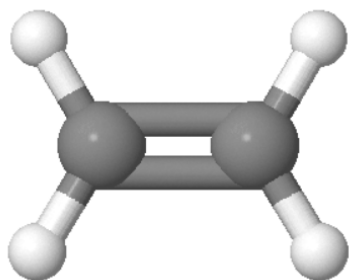
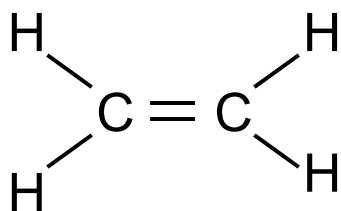
Radicals are electrically neutral but chemically reactive.

OH radical

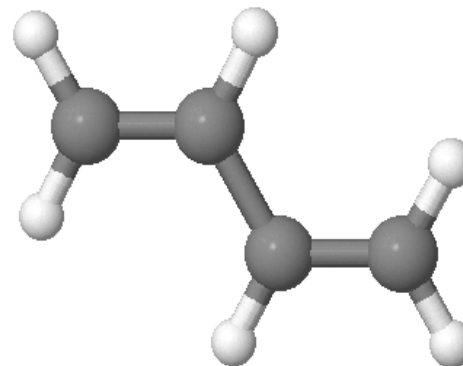
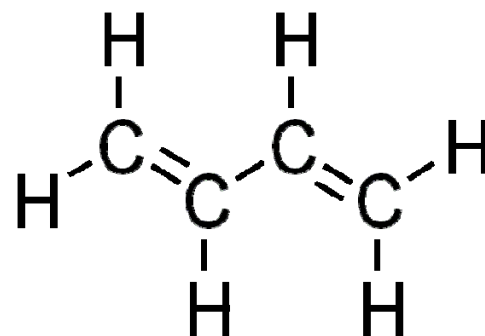
CH₂ methylene radical

Linear chains

ethene



butadiene



$$\Psi_{MO} = c_1 \phi_{2p_z,1}^C + c_2 \phi_{2p_z,2}^C + \dots + c_N \phi_{2p_z,N}^C$$

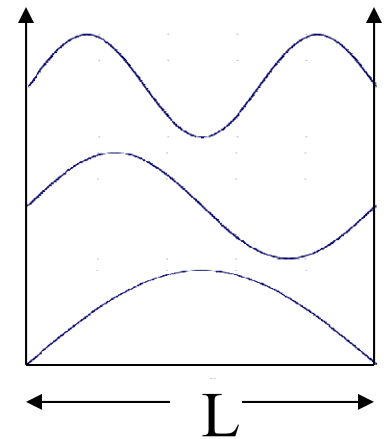
Linear chains

$$\Psi_{MO} = c_1 \phi_{2p_z1}^C + c_2 \phi_{2p_z2}^C + \dots + c_N \phi_{2p_zN}^C$$

Eigen values: $E_j = H_{11} + 2H_{12} \cos\left(\frac{\pi}{N+1} j\right) \quad j = 1, 2, 3 \dots, N$

$$c_{j,n} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi j n}{N+1}\right)$$

Eigen vectors: $\Psi_{MO,j} = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin\left(\frac{\pi j n}{N+1}\right) \phi_{2p_z2}^C$



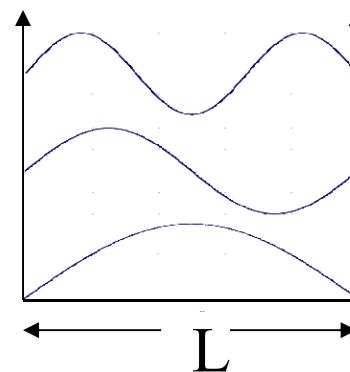
Molecular orbitals of a conjugated chain

The Roothaan equations for a conjugated chain of N atoms have the form,

$$\begin{bmatrix} H_{11} & H_{12} & 0 & \cdots & 0 & 0 \\ H_{12} & H_{11} & H_{12} & 0 & & 0 \\ 0 & H_{12} & H_{11} & H_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & H_{12} & H_{11} & H_{12} \\ 0 & 0 & \cdots & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & \cdots & 0 & 0 \\ S_{12} & 1 & S_{12} & 0 & & 0 \\ 0 & S_{12} & 1 & S_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & S_{12} & 1 & S_{12} \\ 0 & 0 & \cdots & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix} .$$

$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{\pi j}{N+1}\right)}{1 + 2S_{12} \cos\left(\frac{\pi j}{N+1}\right)}$$

$$j = 1, 2, \dots, N.$$



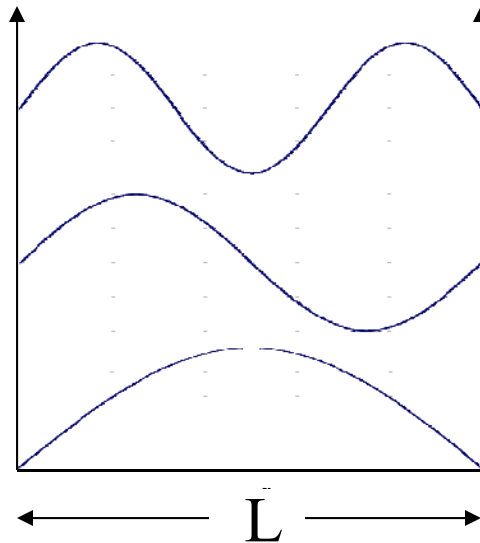
$$\psi_{\text{mo},j} = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin\left(\frac{\pi n j}{N+1}\right) \phi_{pz,n}$$

$$j = 1, 2, \dots, N.$$

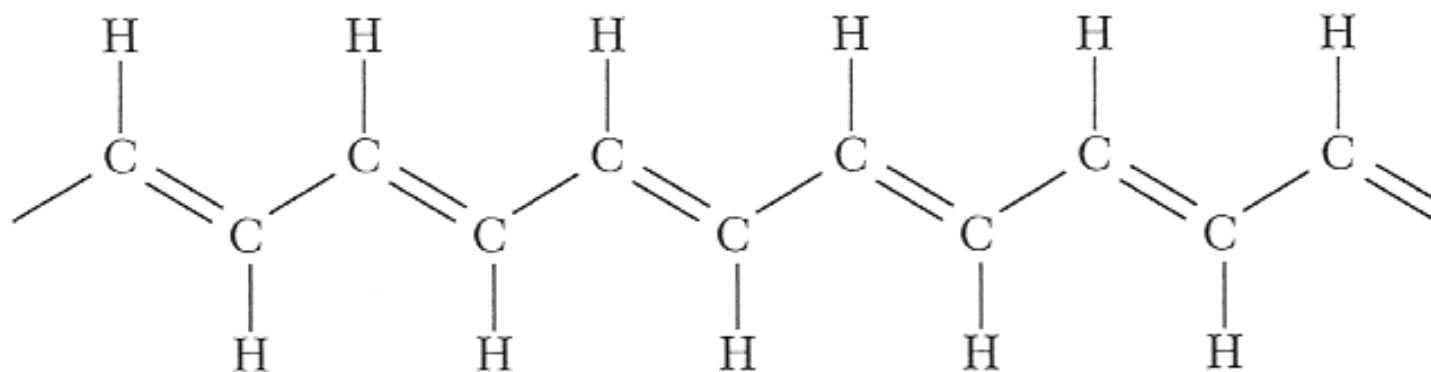
Particles confined to a line

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$
$$n = 1, 2, 3, \dots$$



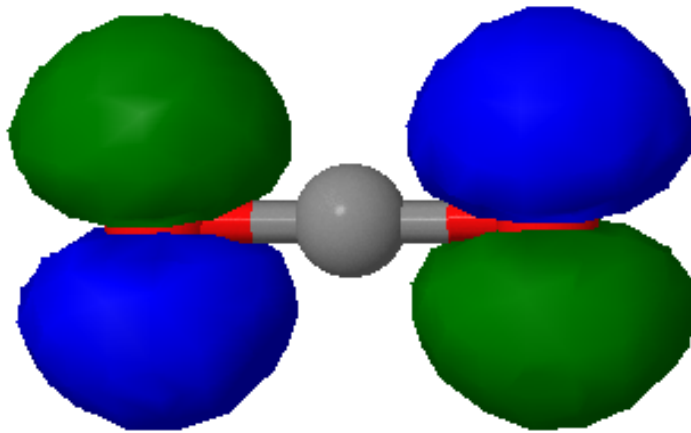
Polyacetylene



Hideki Shirakawa, Alan J. Heeger, and Alan G MacDiarmid
Nobel Prize in Chemistry in 2000

CO2

How were these orbitals calculated and what do the numbers mean?



Model:

Molecular orbitals:

Energy = -15.68642ev

<http://lampx.tugraz.at/~hadley/ss1/skriptum/outline.php>

List of quantum chemistry and solid-state physics software

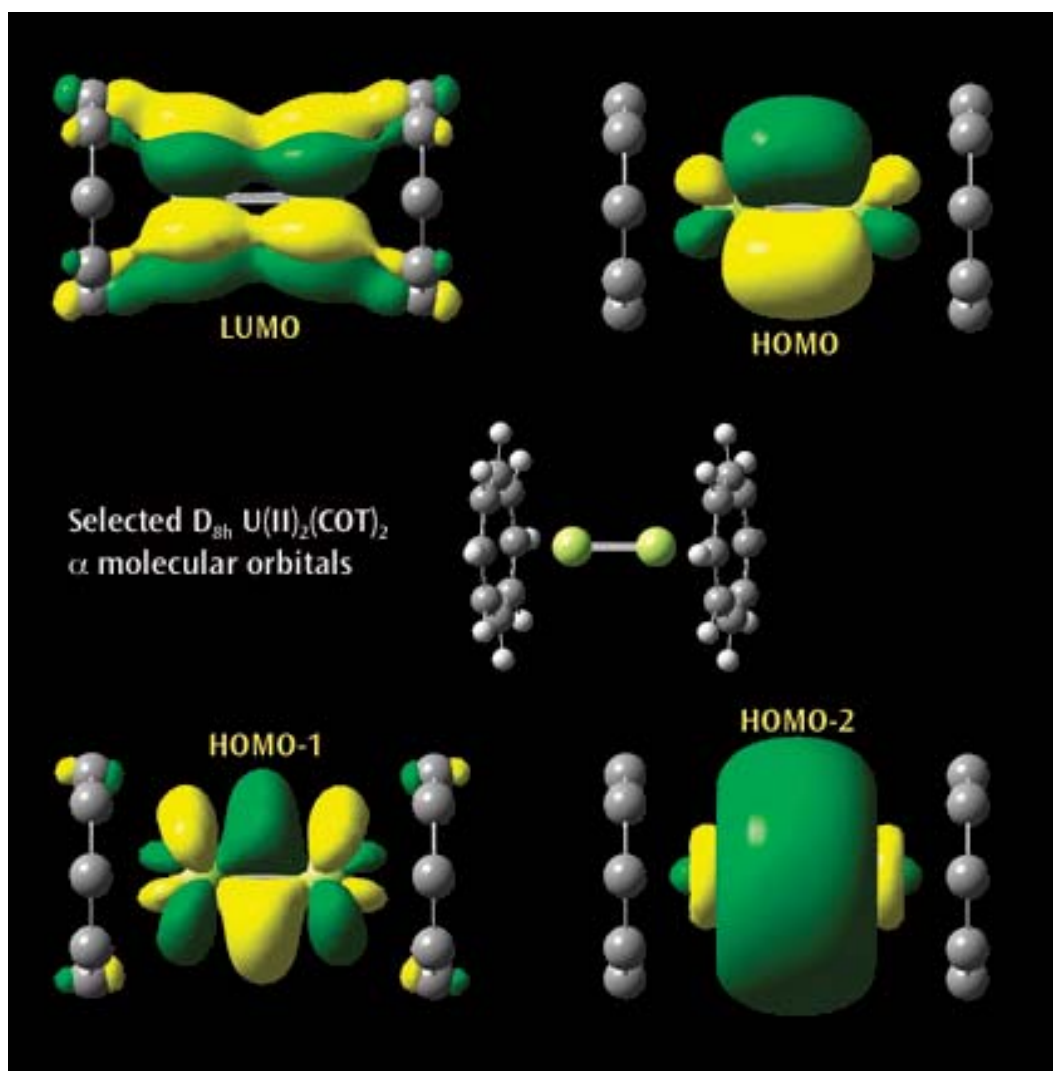
From Wikipedia, the free encyclopedia

Quantum chemistry computer programs are used in [computational chemistry](#) to implement the methods of [quantum chemistry](#). Most include the [Hartree–Fock](#) [post-Hartree–Fock](#) methods. They may also include [density functional theory](#) (DFT), [molecular mechanics](#) or [semi-empirical quantum chemistry methods](#). They are available as both [open source](#) and commercial software. Most of them are large, often containing several separate programs, and have developed over many years.

The following table illustrates the capabilities of the most versatile software packages that show an entry in two or more columns of the table.

| Package | License [†] | Lang. | Basis | Periodic [‡] | Mol. mech. | Semi-emp. | HF | F |
|---|------------------------------------|-----------------------------|--|-----------------------|------------|------------------|------------------|---|
| ABINIT | GPL | Fortran | PW | 3d | Yes | No | No | |
| ACES II | GPL | Fortran | GTO | No | No | No | Yes | |
| ACES III | GPL | Fortran/C++ | GTO | No | No | No | Yes | |
| ADF | Commercial | Fortran | STO | Any | Yes | Yes ⁴ | Yes | |
| Atomistix ToolKit (ATK) | Commercial | C++/Python | NAO/EHT | 3d ⁹ | Yes | Yes | No | |
| BigDFT | GPL | Fortran | Wavelet | Any | Yes | No | Yes | |
| CADPAC | Academic | Fortran | GTO | No | No | No | Yes | |
| CASINO (QMC) | Academic | Fortran 95 | GTO / PW / Spline / Grid / STO | Any | No | No | Yes | |
| CASTEP | Academic (UK) / Commercial | Fortran | PW | 3d | Yes | No | Yes ⁵ | |
| CFOUR | Academic | Fortran | GTO | No | No | No | Yes | |
| COLUMBUS | Academic | Fortran | GTO | No | No | No | Yes | |
| CONQUEST | Academic | Fortran 90 | NAO/Spline | 3d | Yes | No | Yes ⁵ | |
| CP2K | GPL | Fortran 95 | Hybrid GTO / PW | Any | Yes | Yes | Yes | |
| CPMD | Academic | Fortran | PW | Any | Yes | No | Yes | |
| CRYSTAL | Academic (UK) / Commercial | Fortran | GTO | Any | Yes | No | Yes | |
| DACAPO | GPL ? ¹ | Fortran | PW | 3d | Yes | No | No | |
| DALTON | Academic | Fortran | GTO | No | No | No | Yes | |
| DFTB+ ↗ | Academic / Commercial | Fortran 95 | NAO | Any | Yes | Yes | No | |

Gaussian



http://www.gaussian.com/g_prod/gv5b.htm