

Review: Molecules

Start with the full Hamiltonian

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Use the Born-Oppenheimer approximation

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Neglect the electron-electron interactions. H_{elec} is then a sum of H_{MO} .

$$H_{MO} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 |r_1 - r_A|}$$

The molecular orbital Hamiltonian can be solved numerically or by the Linear Combinations of Atomic Orbitals (LCAO)

LCAO example: OH

Guess that the solution to H_{mo} can be written as a linear combination of atomic orbitals. For OH:

$$\psi_{mo} = c_1 \phi_{1s}^H + c_2 \phi_{2s}^O + c_3 \phi_{2px}^O + c_4 \phi_{2py}^O + c_5 \phi_{2pz}^O + \dots$$

$$H\psi_{mo} = E\psi_{mo}$$

Construct the Hamiltonian matrix.

$$\begin{bmatrix}
 \langle \phi_{1s}^H | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{1s}^H | H_{mo} | \phi_{2s}^O \rangle & \dots & \langle \phi_{1s}^H | H_{mo} | \phi_{2pz}^O \rangle \\
 \langle \phi_{2s}^O | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{2s}^O | H_{mo} | \phi_{2s}^O \rangle & & \vdots \\
 \vdots & & \ddots & \\
 \langle \phi_{2pz}^O | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{2pz}^O | H_{mo} | \phi_{2s}^O \rangle & \dots & \langle \phi_{2pz}^O | H_{mo} | \phi_{2pz}^O \rangle
 \end{bmatrix}
 \begin{bmatrix}
 c_1 \\
 c_2 \\
 \vdots \\
 c_5
 \end{bmatrix}
 = E
 \begin{bmatrix}
 \langle \phi_{1s}^H | \phi_{1s}^H \rangle & \langle \phi_{1s}^H | \phi_{2s}^O \rangle & \dots & \langle \phi_{1s}^H | \phi_{2pz}^O \rangle \\
 \langle \phi_{2s}^O | \phi_{1s}^H \rangle & \langle \phi_{2s}^O | \phi_{2s}^O \rangle & & \vdots \\
 \vdots & & \ddots & \\
 \langle \phi_{2pz}^O | \phi_{1s}^H \rangle & \langle \phi_{2pz}^O | \phi_{2s}^O \rangle & & \langle \phi_{2pz}^O | \phi_{2pz}^O \rangle
 \end{bmatrix}
 \begin{bmatrix}
 c_1 \\
 c_2 \\
 \vdots \\
 c_5
 \end{bmatrix}$$

↑
↑

Hamiltonian matrix
Overlap matrix S

Linear combination of atomic orbitals

The overlap matrix $S \approx 1$.

$$\begin{bmatrix} \langle \phi_{1s}^H | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{1s}^H | H_{mo} | \phi_{2s}^O \rangle & \cdots & \langle \phi_{1s}^H | H_{mo} | \phi_{2pz}^O \rangle \\ \langle \phi_{2s}^O | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{2s}^O | H_{mo} | \phi_{2s}^O \rangle & & \vdots \\ \vdots & & \ddots & \\ \langle \phi_{2pz}^O | H_{mo} | \phi_{1s}^H \rangle & \langle \phi_{2pz}^O | H_{mo} | \phi_{2s}^O \rangle & \cdots & \langle \phi_{2pz}^O | H_{mo} | \phi_{2pz}^O \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_5 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_5 \end{bmatrix}$$

This is an eigenvalue problem.

Solve to find the eigenenergies and the coefficients

Molecular orbitals

Construct the many-electron wave function from the molecular orbitals.

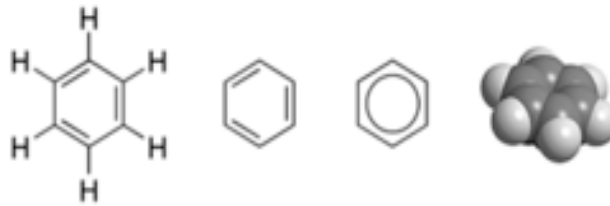
$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{MO1} \uparrow(\vec{r}_1) & \psi_{MO1} \downarrow(\vec{r}_1) & \cdots & \psi_{MO,N} \uparrow(\vec{r}_1) \\ \psi_{MO1} \uparrow(\vec{r}_2) & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{MO1} \uparrow(\vec{r}_N) & \cdots & \cdots & \psi_{MO,N} \uparrow(\vec{r}_N) \end{vmatrix}$$

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Evaluate the energy of the many-electron wave function.

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

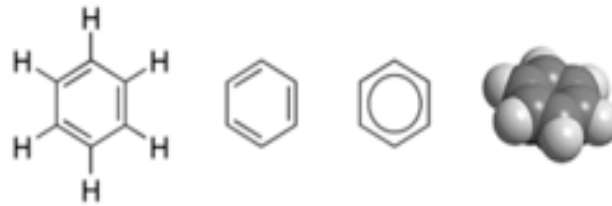
Benzene



Assume the valence molecular orbital is

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

Hückel model benzene



$$\begin{aligned}
 H_{11} &= \langle \phi_{2p_z n}^C | H_{MO} | \phi_{2p_z n}^C \rangle \\
 H_{12} &= \langle \phi_{2p_z n}^C | H_{MO} | \phi_{2p_z n+1}^C \rangle
 \end{aligned}$$

$$\begin{bmatrix}
 H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\
 H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\
 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\
 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\
 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\
 H_{12} & 0 & 0 & 0 & H_{12} & H_{11}
 \end{bmatrix}$$

Hückel model: matrix elements of next nearest neighbors = 0.
 Overlap matrix $S=1$.

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

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

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

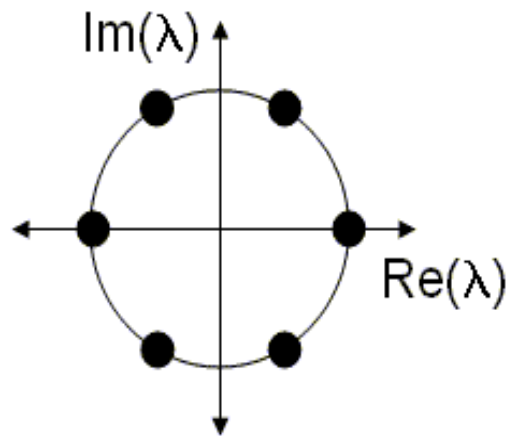
$$\mathbf{T}^{-1} \vec{u} = \mathbf{T}^{N-1} \vec{u} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix}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

Eigen values of the translation operator

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

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

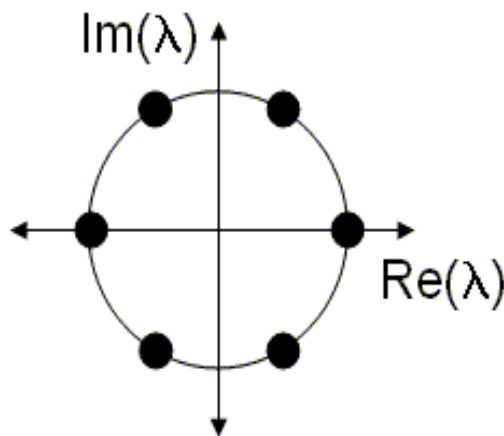
$$\lambda^N = 1$$



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

Eigen vectors of the translation operator

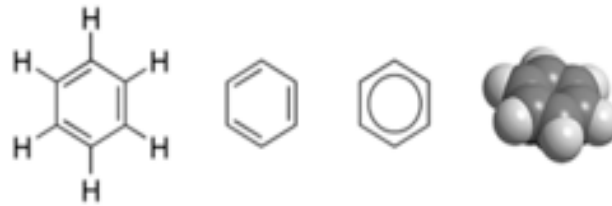
$$T = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$



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

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

Hückel model benzene



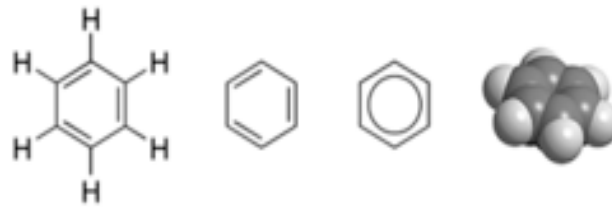
$$H_{11} = \langle \phi_{2p_z n}^C | H_{MO} | \phi_{2p_z n}^C \rangle$$

$$H_{12} = \langle \phi_{2p_z n}^C | H_{MO} | \phi_{2p_z n+1}^C \rangle$$

$$\begin{bmatrix} H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\ 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\ 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\ 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & 0 & 0 & H_{12} & H_{11} \end{bmatrix}$$

Hückel model: matrix elements of next nearest neighbors = 0.
Overlap matrix $S=1$.

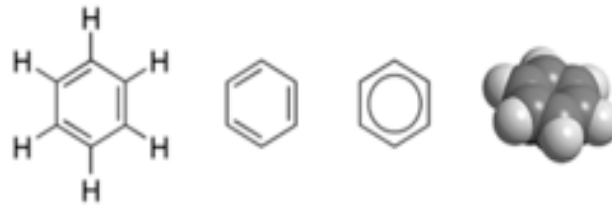
Hückel model benzene



$$\begin{bmatrix}
 H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\
 H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\
 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\
 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\
 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\
 H_{12} & 0 & 0 & 0 & H_{12} & H_{11}
 \end{bmatrix} = H_{11} \mathbf{T}^N + H_{12} (\mathbf{T} + \mathbf{T}^{-1})$$

The Hamiltonian matrix and the translation operator commute and have the same eigenvectors.

Hückel model benzene



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

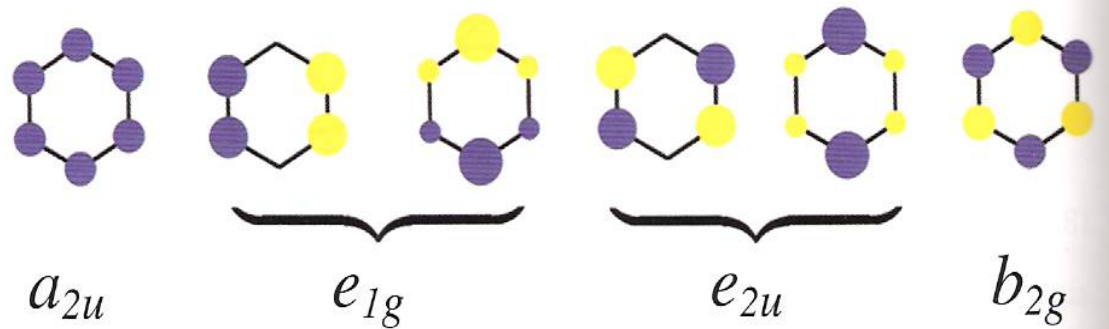
$$e^{i\pi j/3} + e^{-i\pi j/3} = 2 \cos\left(\frac{\pi j}{3}\right)$$

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

Hückel model benzene

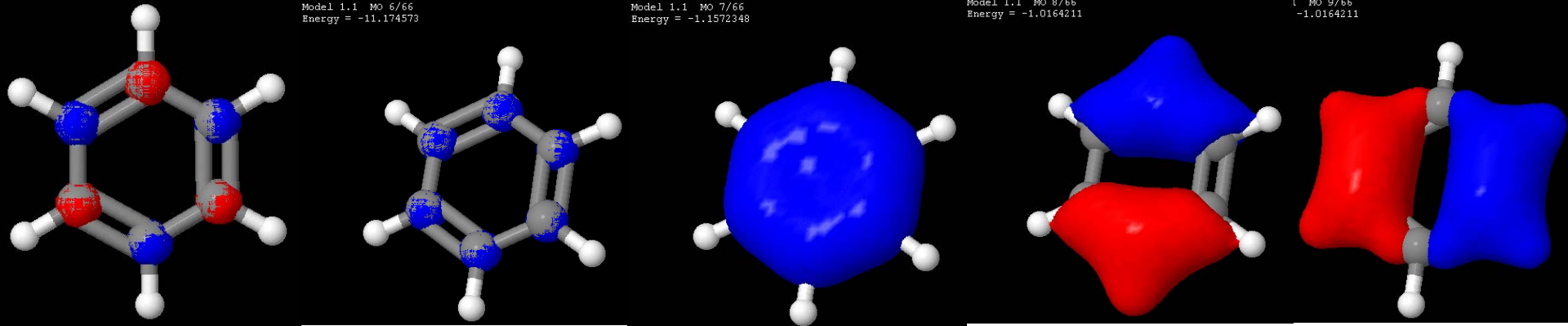
$$\psi_j = \varphi_{2p_z1}^C + e^{i\pi j/3} \varphi_{2p_z2}^C + e^{i2\pi j/3} \varphi_{2p_z3}^C + e^{i\pi j} \varphi_{2p_z4}^C + e^{-i2\pi j/3} \varphi_{2p_z5}^C + e^{-i\pi j/3} \varphi_{2p_z6}^C$$

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



from: Blinder, Introduction to Quantum Mechanics

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



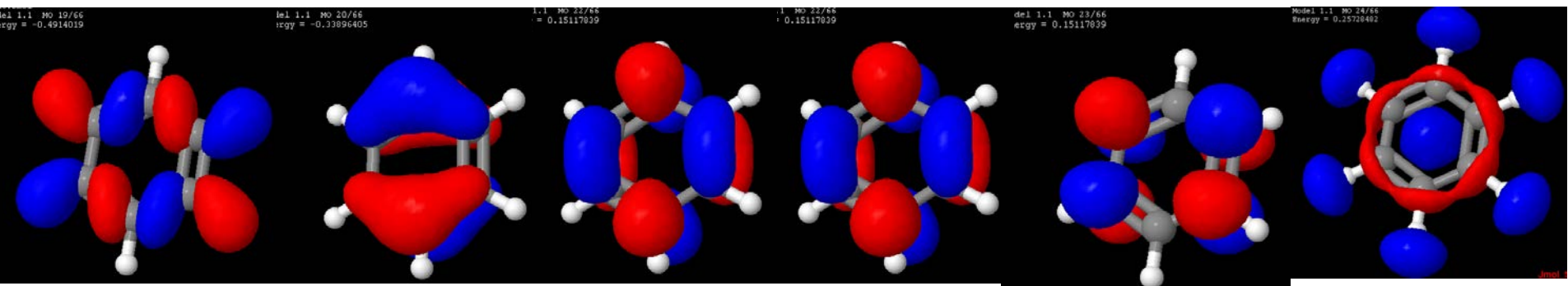
1

6

7

8

9



19

20

21=homo

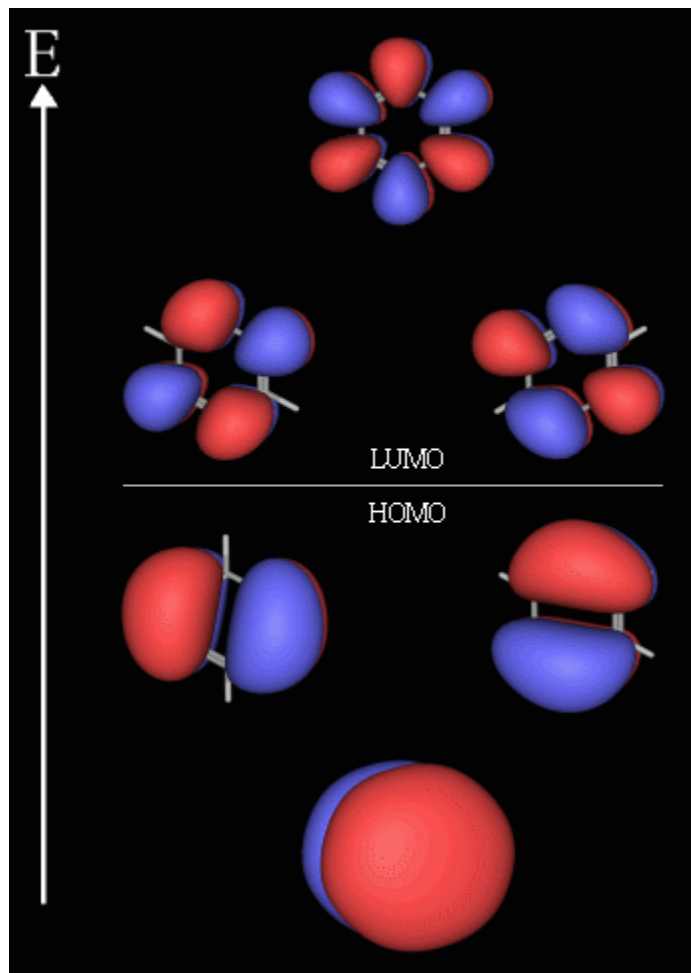
22=lumo

23

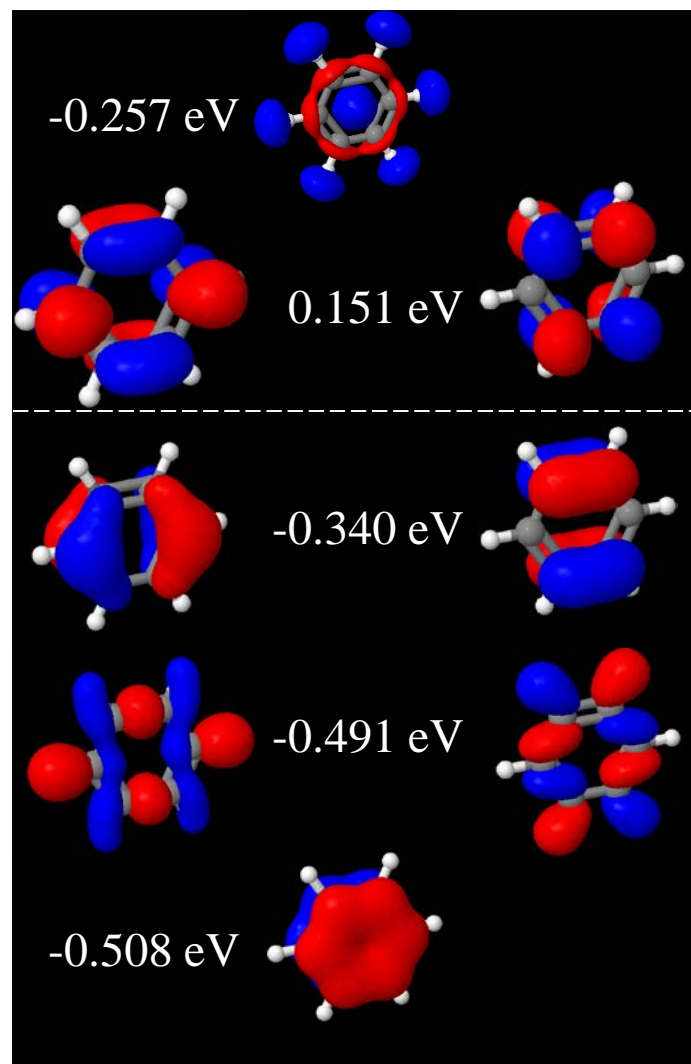
24

Molecular orbitals benzene

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



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

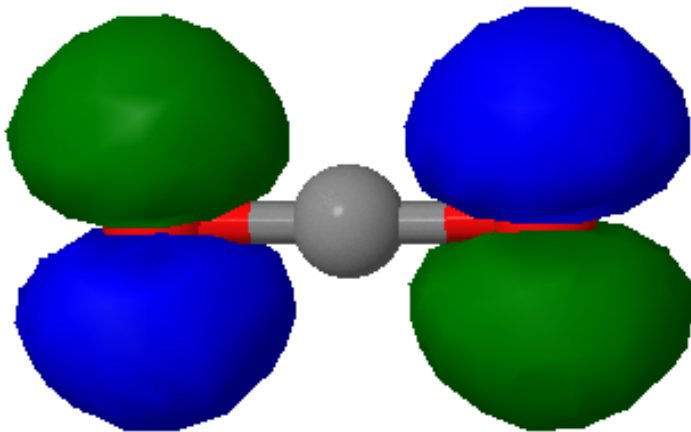


Some *e-e* effects included

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

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

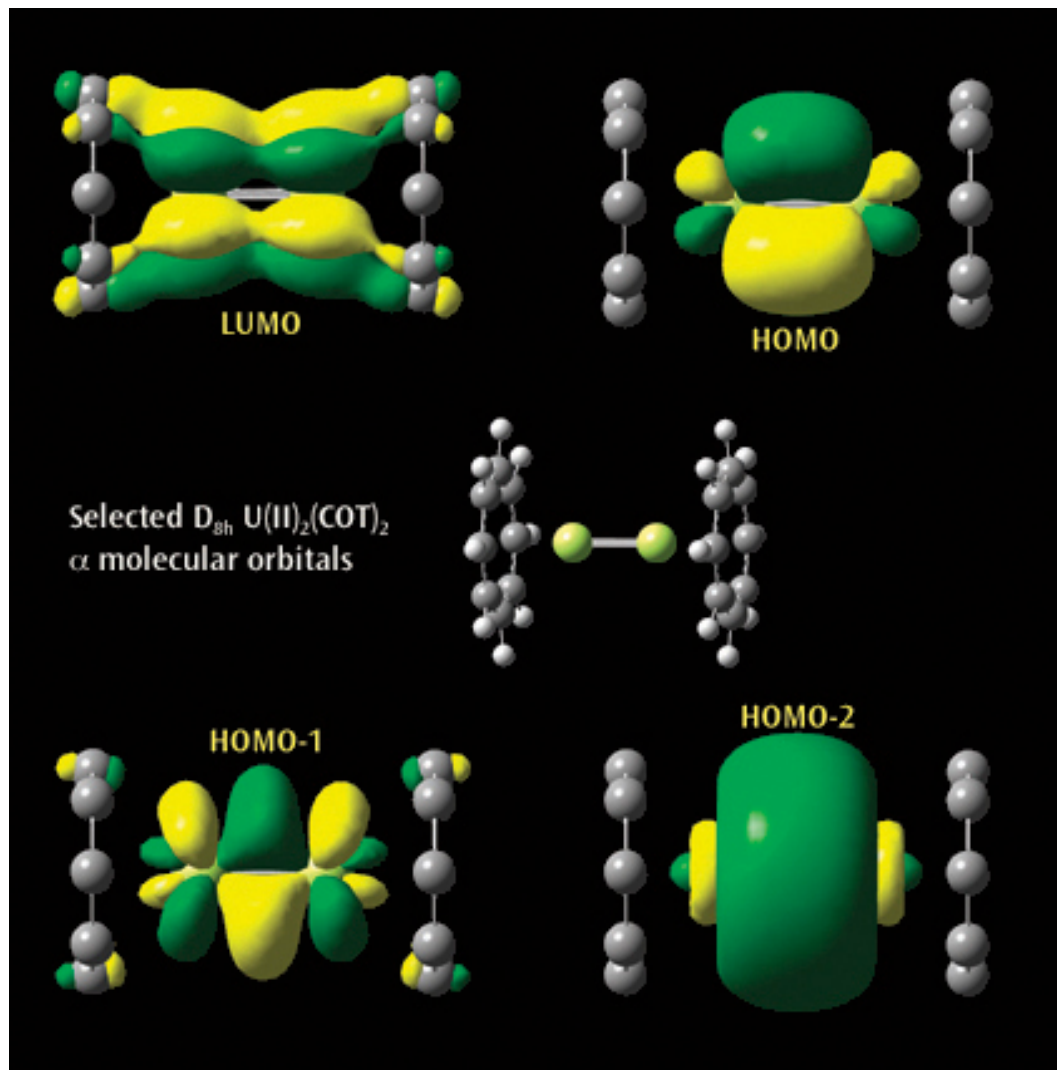
From Wikipedia, the free encyclopedia

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](#). The programs 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	P
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



Hückel model rings

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

Assume $S_{11} = S_{22} = 1$ $S_{12} = 0$

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

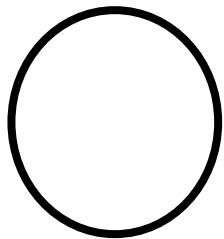
Hückel model, rings

The general formula for N atoms in a ring is:

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

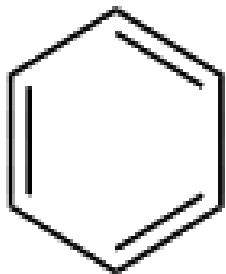
$$\psi_{MO,j} = \frac{1}{\sqrt{N}} \sum_{n=1}^N \exp\left(\frac{i2\pi nj}{N}\right) \phi_{2p_z n}^C \quad j = 1, 2, \dots, N$$

Particles confined to a ring



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

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

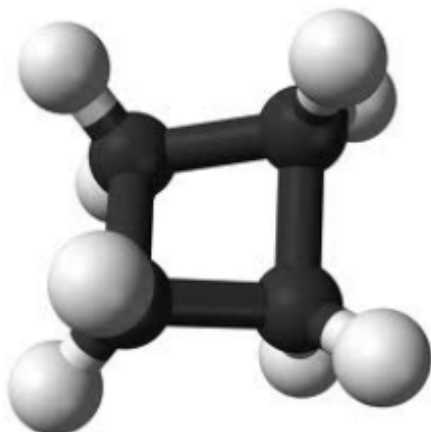
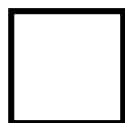


$$E_n = \frac{\hbar^2 n^2}{2mR^2}$$

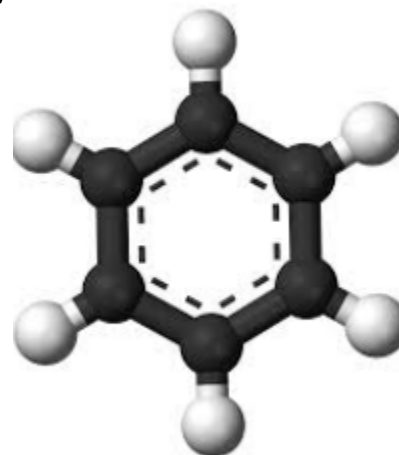
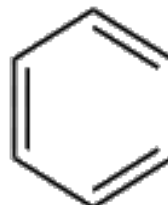
Aromatic molecules obey Hückel's $4n + 2$ rule
Molecules that don't obey the $4n+2$ rule are radicals

Particles confined to a ring

cyclobutane



benzene



$$4n + 2$$

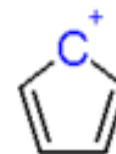
Antiaromaticity

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*.



A



B



Radicals

Molecules are most stable with a closed shell configuration.

Ar

H₂O 10 electrons

NH₃

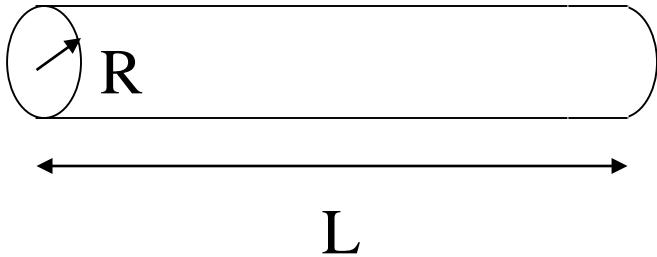
CH₄

Radicals are electrically neutral but chemically reactive.

OH radical

CH₂ methylene radical

Particles confined to a tube



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

$$\psi_n = \frac{e^{in\theta} e^{ikx}}{\sqrt{\pi RL}}$$

$$n = 0, \pm 1, \pm 2, \dots \quad k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$$

$$E_{n,k} = \frac{\hbar^2 n^2}{2mR^2} + \frac{\hbar^2 k^2}{2m}$$

$4n + 2$ rule

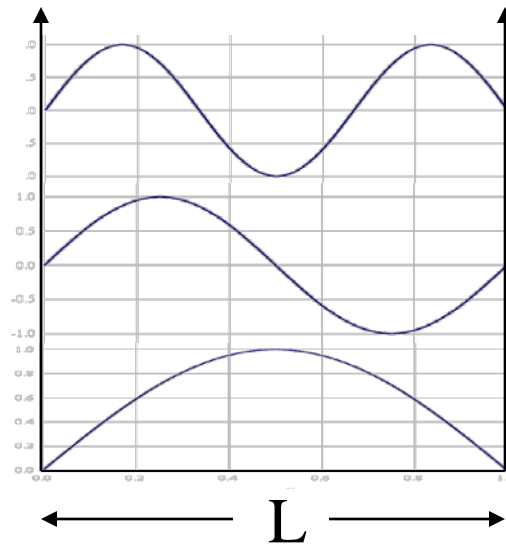


Particles confined to a line

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

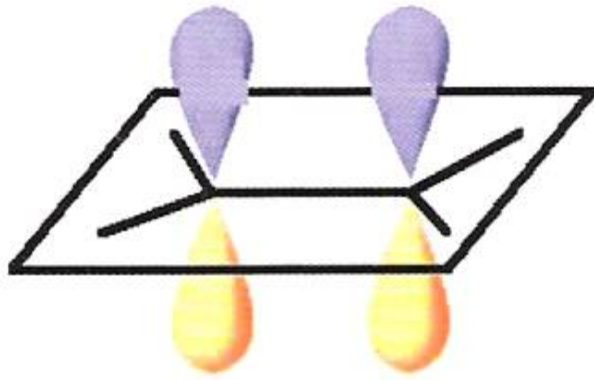
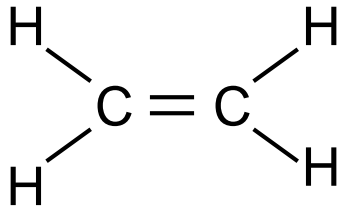
$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$n = 1, 2, 3, \dots$$

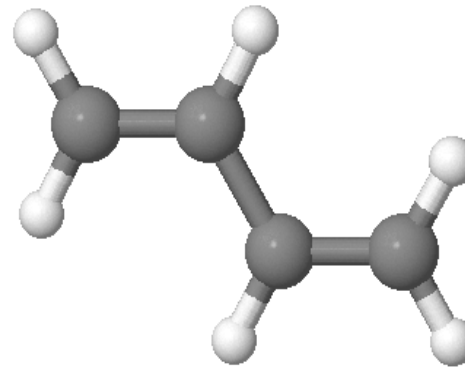
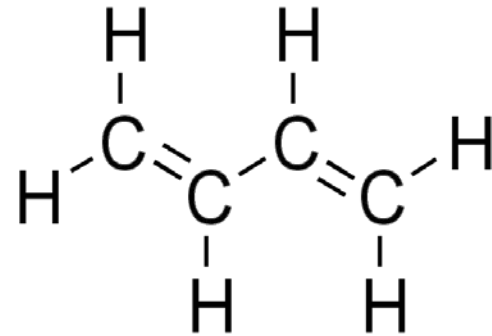


Linear chains

ethene



butadiene



Hückel model - linear chains

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

Assume $S_{11} = S_{22} = 1$ $S_{12} = 0$

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

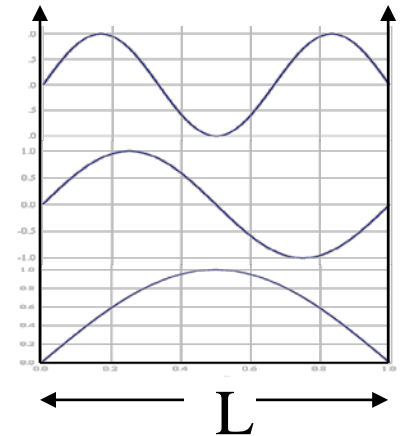
Hückel model - linear chains

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

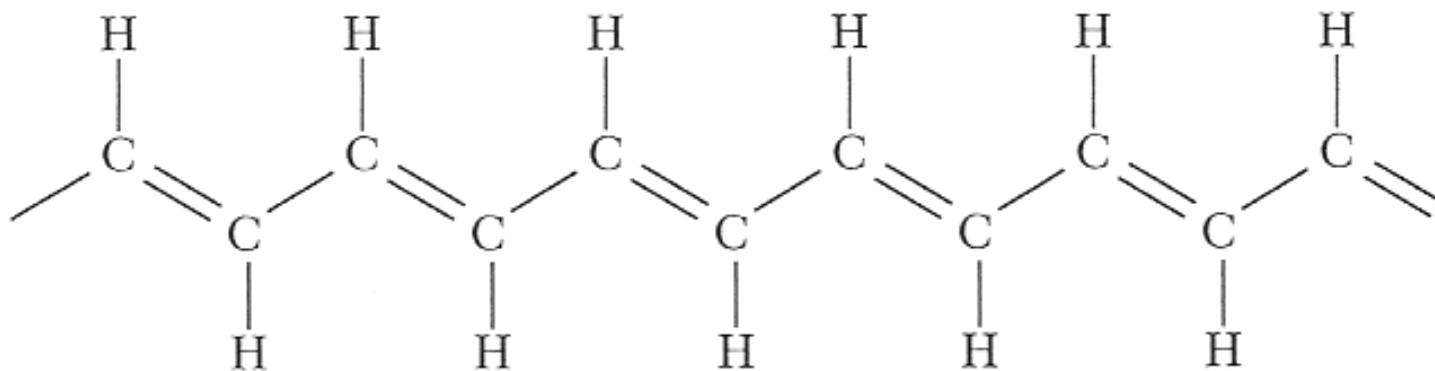
Eigen values: $E_j = H_{11} + 2H_{12} \cos\left(\frac{\pi}{N+1} j\right) \quad j = 1, 2, 3, \dots, N$

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

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



Polyacetylene



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