Molecular orbitals

Homonuclear diatomic molecules

H_2, N_2, O_2, ...

$$H_{\mathrm{mo}} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_A|} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_B|}$$

All homonuclear diatomic molecules use the molecular orbitals of H_2.

$$\psi_{mo} = c_1\phi^Z_{1s,A} + c_2\phi^Z_{1s,B} + c_3\phi^Z_{2s,A} + c_4\phi^Z_{2s,B} + c_5\phi^Z_{2p_x,A} + c_6\phi^Z_{2p_x,B} + \cdots$$

The Hamiltonian matrix is as large as the number of atomic orbitals in the molecular orbital sum.

Homonuclear diatomic molecules

$$\psi_{\mathrm{mo}} = \sum_{p=1}^{N} c_p \phi_p$$

$$H_{\mathrm{mo}} \psi_{\mathrm{mo}} = E \psi_{\mathrm{mo}}$$

Roothaan equations:

$$\begin{aligned}
\langle \phi_1 | H_{\mathrm{mo}} | \psi_{\mathrm{mo}} \rangle &= E \langle \phi_1 | \psi_{\mathrm{mo}} \rangle \\
\langle \phi_2 | H_{\mathrm{mo}} | \psi_{\mathrm{mo}} \rangle &= E \langle \phi_2 | \psi_{\mathrm{mo}} \rangle \\
&\vdots \\
\langle \phi_N | H_{\mathrm{mo}} | \psi_{\mathrm{mo}} \rangle &= E \langle \phi_N | \psi_{\mathrm{mo}} \rangle
\end{aligned}$$

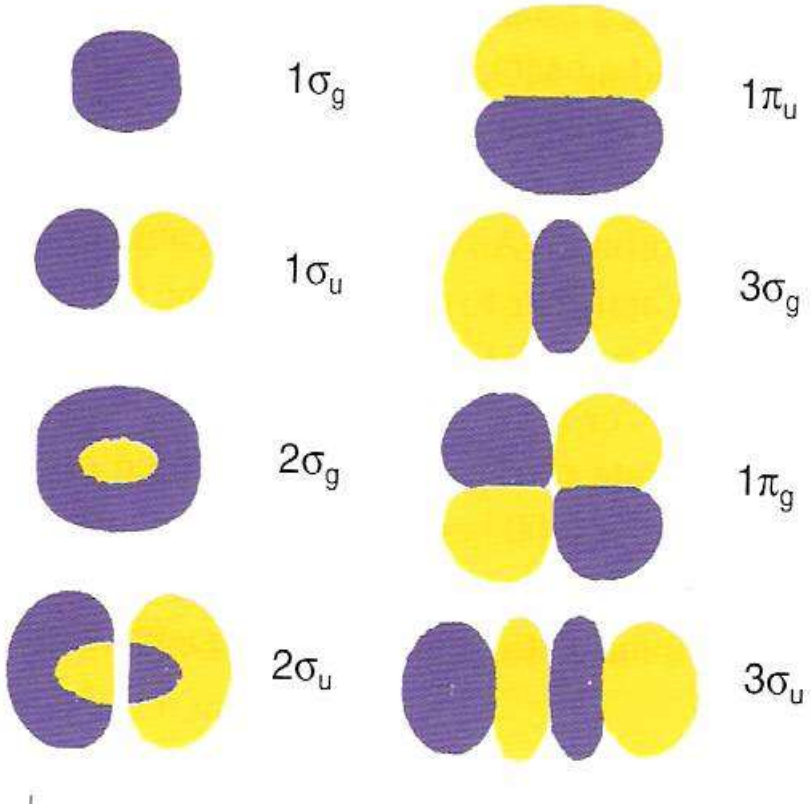
$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}$$

As many molecular orbitals as unknow coefficients *c*

Homonuclear diatomic molecules

All homonuclear diatomic molecules use the molecular orbitals of H_2.

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g \sim 1\pi_u < 1\pi_g < 3\sigma_u$$

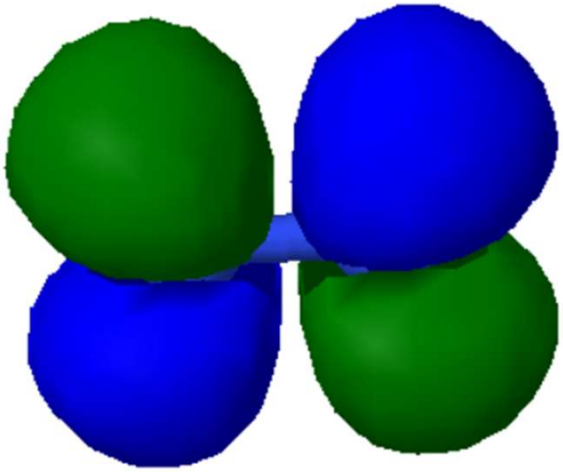


g → inversion symmetry

from: Blinder, Introduction to Quantum Mechanics

N2

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



Model: Ball and Stick Spacefill

Molecular orbitals: 1 2 3 4 5 6 7=HOMO 8=LUMO 9

Energy = 0.70042ev

http://lampx.tugraz.at/~hadley/ss1/molecules/N2/N2.php

number of electron pairs shared

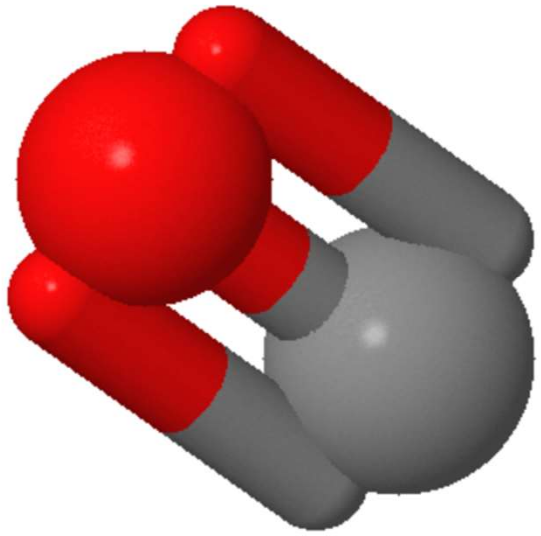
TABLE 11.1 ▶ Homonuclear Diatomic Molecules

Molecule	Electron Configuration	Bond Order	D_e/eV	R_e/Å
H_2^+	$1\sigma_g \ {}^2\Sigma_g^+$	0.5	2.79	1.06
H_2	$1\sigma_g^2 \ {}^1\Sigma_g^+$	1	4.75	0.741
He_2	$1\sigma_g^2 1\sigma_u^2 \ {}^1\Sigma_g^+$	0	0.0009[a]	3.0
	$1\sigma_g^2 1\sigma_u 2\sigma_g \ {}^3\Sigma_u^+$ [b]	1	2.6	1.05
He_2^+	$1\sigma_g^2 1\sigma_u \ {}^2\Sigma_u^+$	0.5	2.5	1.08
Li_2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \ {}^1\Sigma_g^+$	1	1.07	2.67
Be_2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 \ {}^1\Sigma_g^+$	0	0.1	2.5
B_2	$\ldots 1\pi_u^2 \ {}^3\Sigma_g^-$ [c]	1	3.0	1.59
C_2	$\ldots 1\pi_u^4 \ {}^1\Sigma_g^+$	2	6.3	1.24
N_2	$\ldots 1\pi_u^4 3\sigma_g^2 \ {}^1\Sigma_g^+$	3	9.91	1.10
N_2^+	$\ldots 1\pi_u^4 3\sigma_g \ {}^2\Sigma_g^+$	2.5	8.85 [d]	1.12
O_2	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2 \ {}^3\Sigma_g^-$ [c,e]	2	5.21	1.21
O_2^+	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g \ {}^2\Pi_g$	2.5	6.78 [d]	1.12
F_2	$\ldots 1\pi^4 3\sigma^2 1\pi^4 \ {}^1\Sigma^+$	1	1.66	1.41

from: Blinder, Introduction to Quantum Mechanics

Molecular orbitals of carbon monoxide determined by LCAO

Carbon monoxide CO consists of one carbon atom and one oxygen atom. The bond length is 1.128 Å.

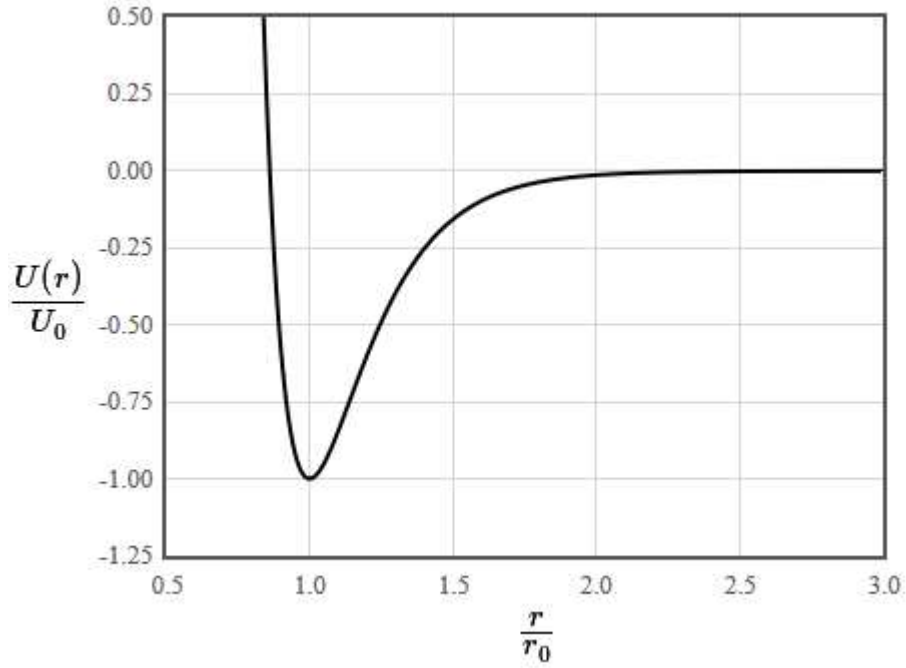


Model: Ball and Stick | Spacefill

JSmol

Bond potentials

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

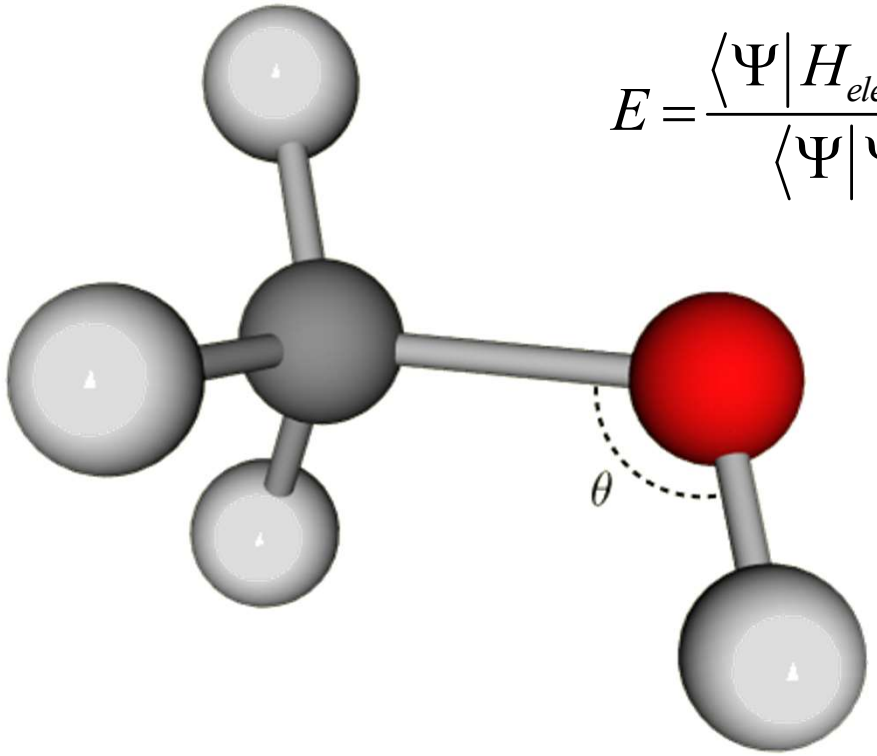


Calculate the energies for different atomic distances.
The minimum yields the bond length and bond strength.

Boondlength (nm) and bond energy (eV)					
Bond	Length	Energy	Bond	Length	Energy
H--H	0.074	4.52	H--C	0.109	4.28
C--C	0.154	3.61	H--N	0.101	4.05
C=C	0.134	6.36	H--F	0.092	5.89
C≡C	0.120	8.70	H--O	0.096	3.79
C--O	0.143	3.73	H--Cl	0.127	4.48
C--S	0.182	2.82	H--Br	0.141	3.79
C--F	0.135	5.06	H--I	0.161	3.09
C--Cl	0.177	3.42	N--N	0.145	1.76
C--Br	0.194	2.98	I--I	0.267	1.57
C--I	0.214	2.24	O--O	0.148	1.50
C--N	0.147	3.19	O=O	0.121	5.16
N--N	0.145	1.76	N≡N	0.110	9.79
O--O	0.148	1.50	Cl-Cl	0.199	2.52
F--F	0.142	1.64	Br-Br	0.228	2.00

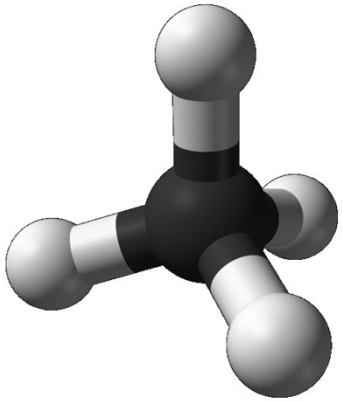
Bond angles

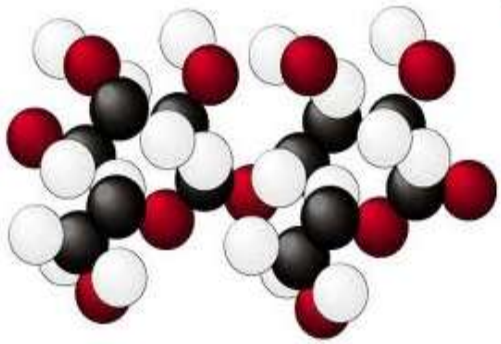
Find the angle that minimizes the energy.



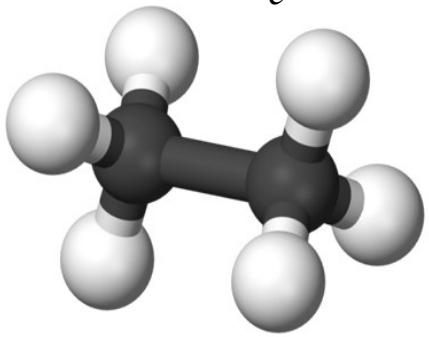
$$E = \frac{\langle \Psi | H_{elec} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

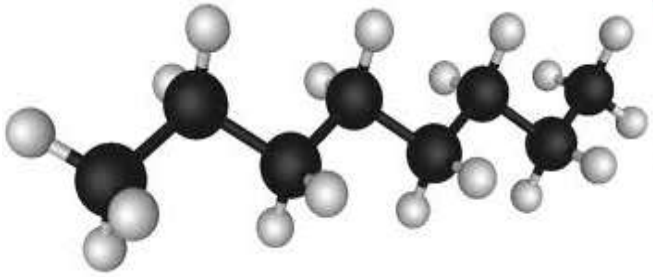
Shape of a molecule



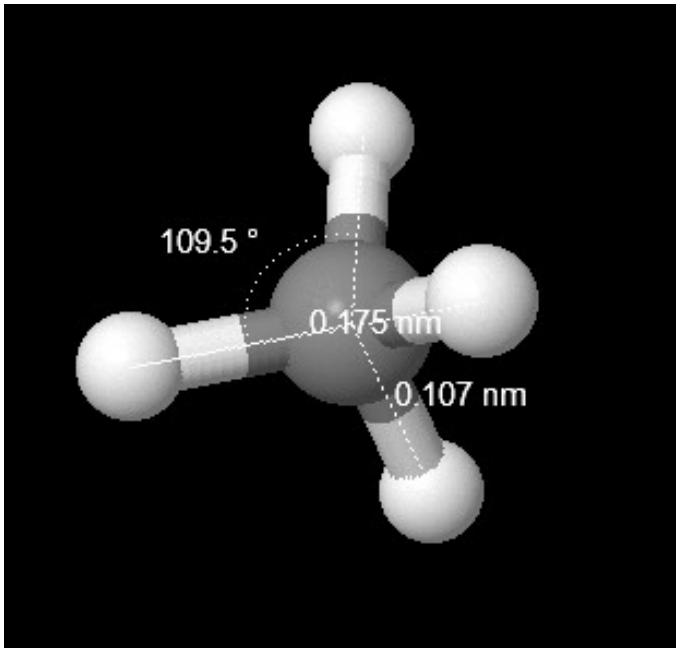


$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}}$$





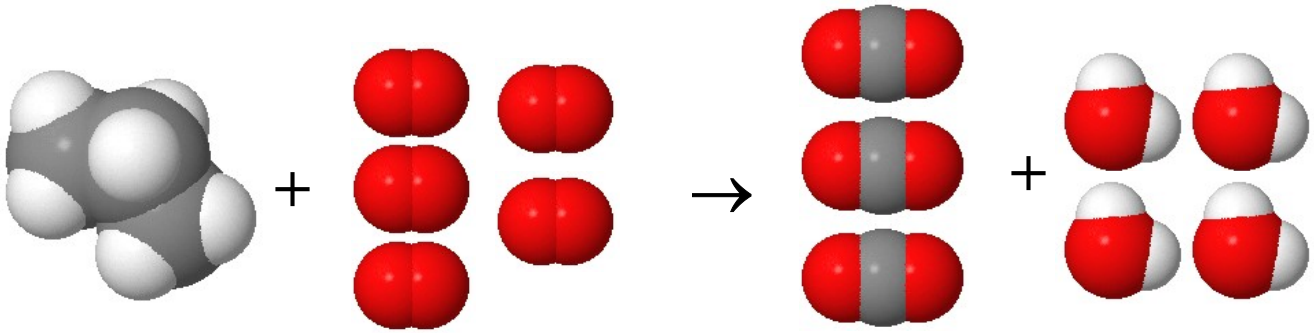
Shape of a molecule



In Jmol, double click to start and stop a measurement.

http://lampx.tugraz.at/~hadley/ss1/molecules/moleculeviewer/viewer.php

Chemical reactions



$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O + \text{Energy}$$

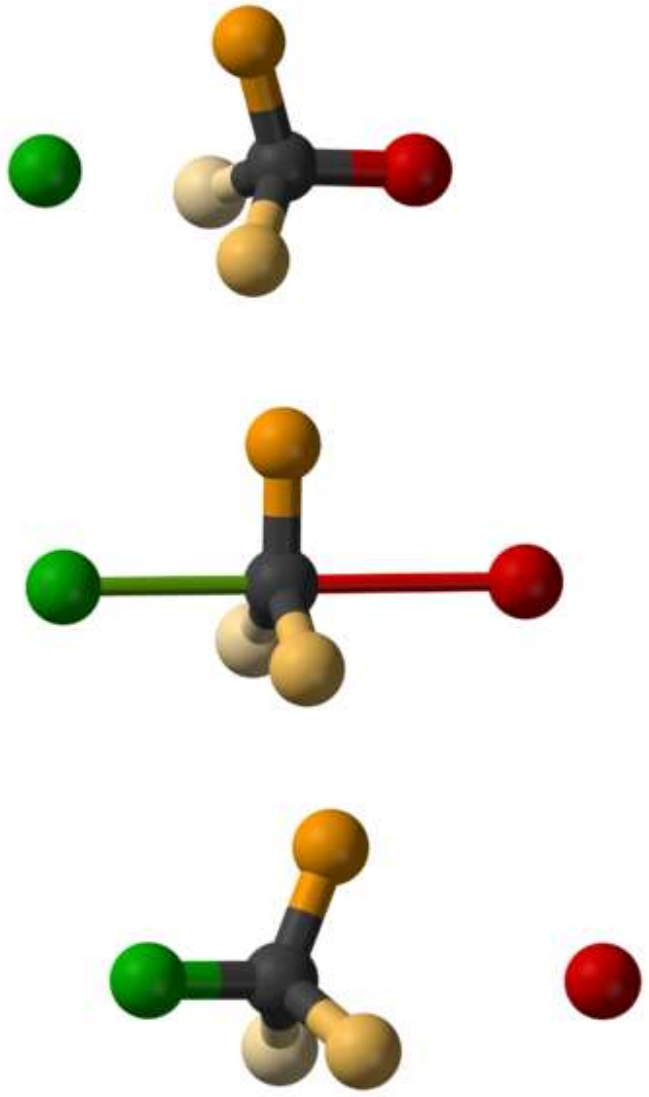
Propane Oxygen Carbon dioxide Water

It is possible to calculate if the reaction is endothermic or exothermic.

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

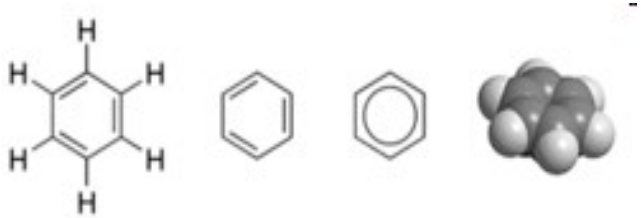
Chemical reactions

To calculate the speed of a chemical reaction, solve the time-dependent Schrödinger equation.



http://en.wikipedia.org/wiki/File:Walden-inversion-3D-balls.png

Benzene



42 electrons

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

36 relevant atomic orbitals

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

Benzene

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

42 electrons
36 relevant atomic orbitals

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

0

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

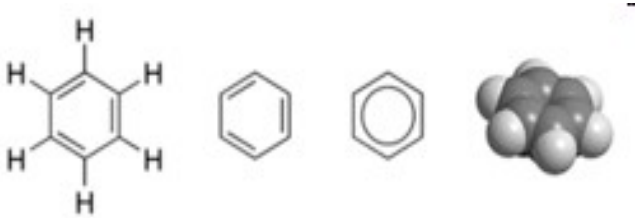
0

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

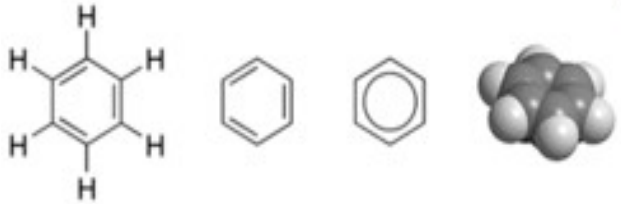


Assume the valence molecular orbital is

$$\Psi_{MO} = c_1\phi^C_{2p_z1} + c_2\phi^C_{2p_z2} + c_3\phi^C_{2p_z3} + c_4\phi^C_{2p_z4} + c_5\phi^C_{2p_z5} + c_6\phi^C_{2p_z6}$$

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

Benzene



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

$$H_{ij} = \langle \phi^C_{2p_z}(\vec{r} - \vec{r}_i) | H_{\text{mo}} | \phi^C_{2pz}(\vec{r} - \vec{r}_j) \rangle \qquad \text{and} \qquad S_{ij} = \langle \phi^C_{2p_z}(\vec{r} - \vec{r}_i) | \phi^C_{2pz}(\vec{r} - \vec{r}_j) \rangle$$

Translation operator

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

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

T and T^2 have the same eigenvectors

Translation operator

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

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

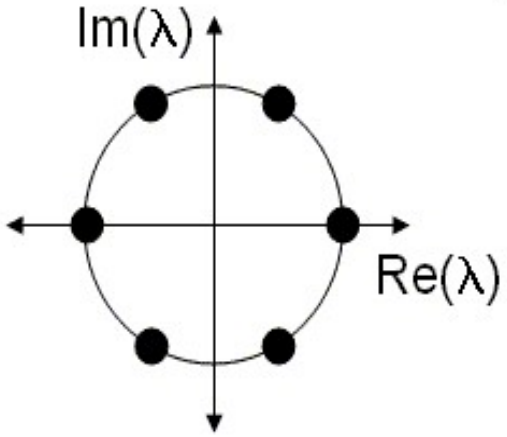
$$\mathrm{T}^{-1}\vec{u} = \mathrm{T}^{N-1}\vec{u} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} =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

Eigen values of the translation operator

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

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

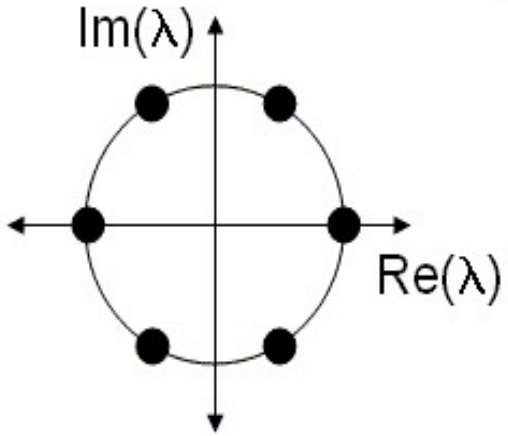
$$\lambda^N = 1$$



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

Eigen vectors of the translation operator

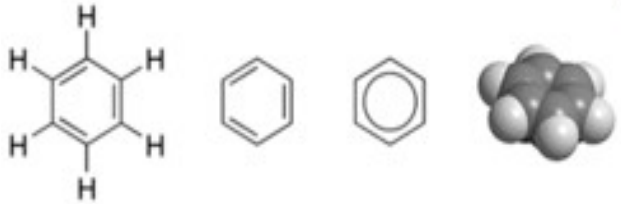
$$T=\begin{bmatrix}0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\end{bmatrix}$$



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

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

Benzene



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

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

Benzene

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

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

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

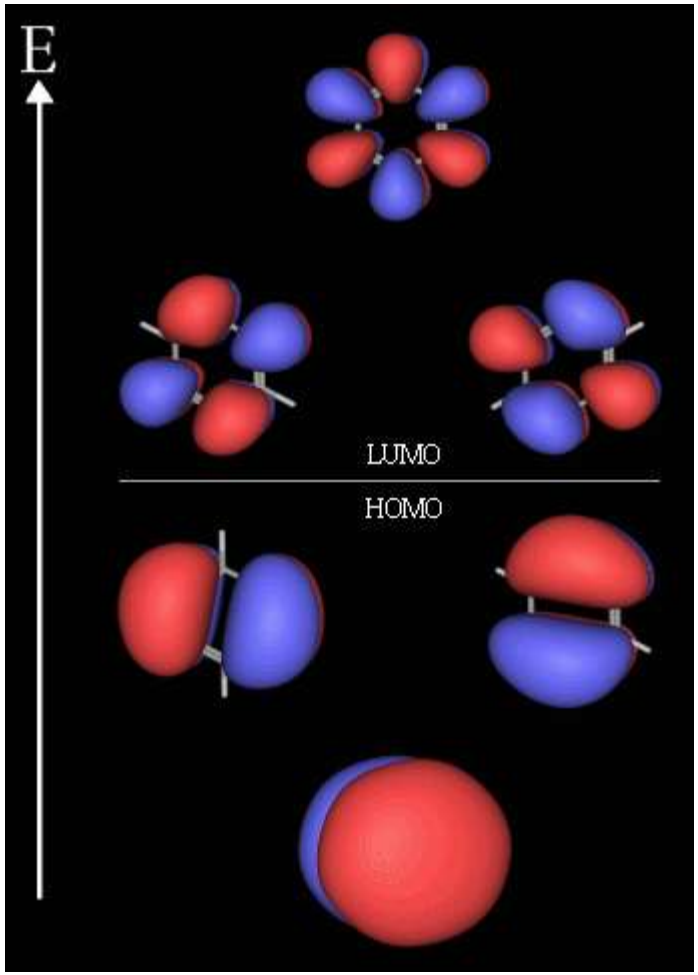
Benzene

$$\psi_j = \varphi^C_{2p_z 1} + e^{i\pi j/3}\varphi^C_{2p_z 2} + e^{i2\pi j/3}\varphi^C_{2p_z 3} + e^{i\pi j}\varphi^C_{2p_z 4} + e^{-i2\pi j/3}\varphi^C_{2p_z 5} + e^{-i\pi j/3}\varphi^C_{2p_z 6}$$

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

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

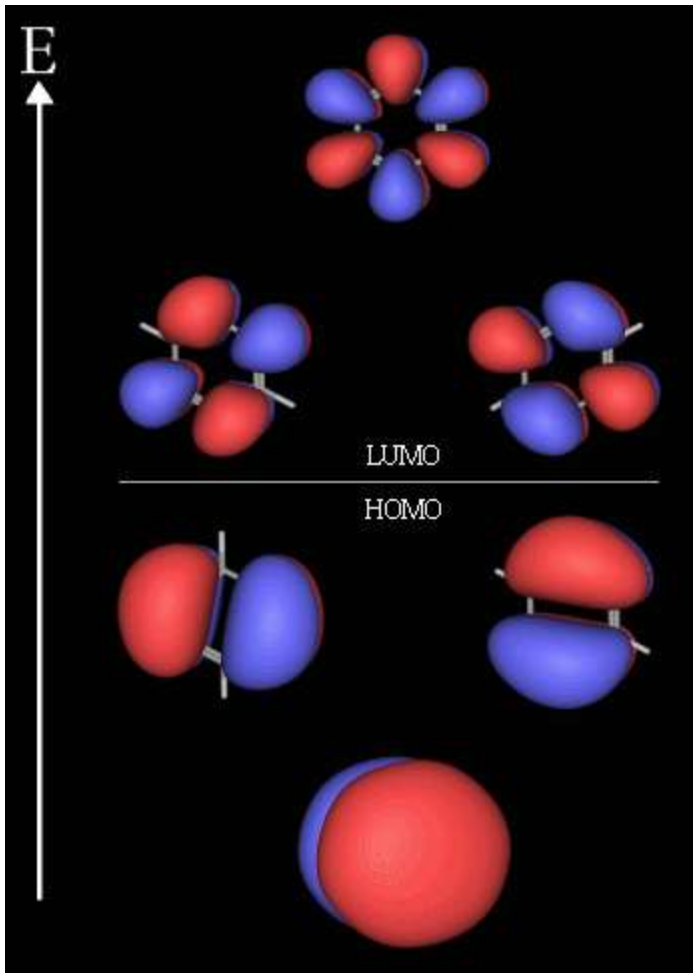
$$j = 1, 2, \cdots, 6.$$

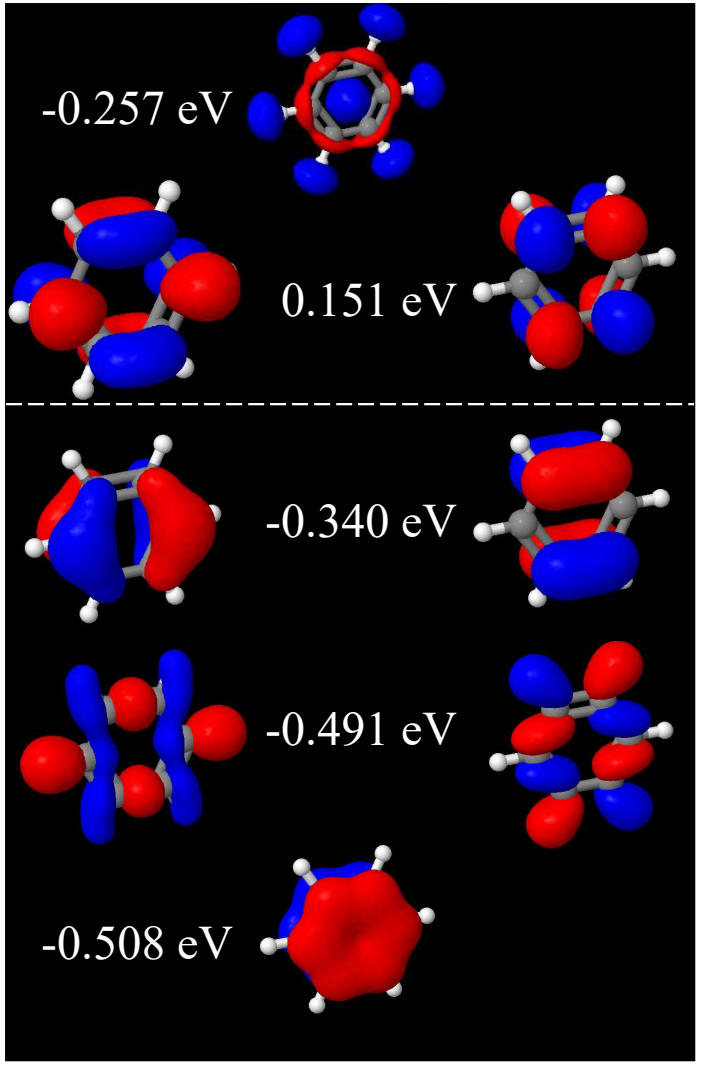


http://www.chemcomp.com/journal/molorbs.htm

Molecular orbitals benzene

http://www.chemcomp.com/journal/molorbs.htm





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

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

Molecular orbitals of a conjugated ring

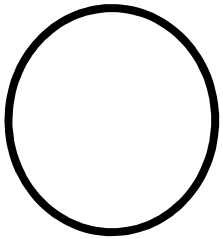
The Roothaan equations for a conjugated ring of N atoms have the form,

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

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

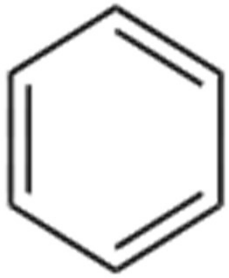
$$\psi_{\mathrm{mo},j} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \exp\left(\frac{i2\pi nj}{N}\right) \phi^{C}_{2pz}(\vec{r} - \vec{r}_n) \qquad j = 1, 2, \cdots, N.$$

Particles confined to a ring



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

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



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

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