

Sensing is life

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Sensor Innovation Challenge

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1st prize: 3.000€ 2nd prize: 2.000€, 3rd prize: 1.000€



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Sensor Innovation Challenge – SENSOR FUSION

Imagine the impossible

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- ❖ Summer semester 2022
- ❖ Register now @TU Graz online:
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- ❖ Supported by the Lecture
Selected Topics of Sensors and Actuators,
Prof. Dr. Alexander Bergmann
- ❖ For Master students of: Electrical Engineering,
Physics, Information & Computer Engineering,
Biomedical Engineering

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Molecules

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)

Molecular orbitals of H₂⁺

The Hamiltonian for H₂⁺ is,

$$H_{\text{mo}}^{H_2} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_B|}$$

\vec{r}_A and \vec{r}_B are the positions of the protons.

$$\psi_{\text{mo}} = c_1 \phi_{1s,A}^H + c_2 \phi_{1s,B}^H + \dots$$

Valence bond theory

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

$$H_{\text{vb}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{Z_{ai} e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_{ai}|} = \sum_i H_{\text{atom}_i}$$

Heitler–London theory

$$H_{\text{vb}} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_a|} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_2 - \vec{r}_b|}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi_{1s}(\vec{r}_1 - \vec{r}_a) \phi_{1s}(\vec{r}_2 - \vec{r}_b)$$

↑
Need to antisymmetrize

Heitler–London theory

$$\Psi_{\uparrow\uparrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \uparrow (\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \uparrow (\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \uparrow (\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \uparrow (\vec{r}_2 - \vec{r}_b) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a)) \uparrow (\vec{r}_1) \uparrow (\vec{r}_2),$$

$$\Psi_{\downarrow\downarrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \downarrow (\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \downarrow (\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \downarrow (\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \downarrow (\vec{r}_2 - \vec{r}_b) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a)) \downarrow (\vec{r}_1) \downarrow (\vec{r}_2),$$

$$\Psi_{\uparrow\downarrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \uparrow (\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \downarrow (\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \uparrow (\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \downarrow (\vec{r}_2 - \vec{r}_b) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a) \uparrow (\vec{r}_1) \phi_{1s}^H(\vec{r}_2 - \vec{r}_b) \downarrow (\vec{r}_2) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b) \downarrow (\vec{r}_1) \phi_{1s}^H(\vec{r}_2 - \vec{r}_a) \uparrow (\vec{r}_2)),$$

$$\Psi_{\downarrow\uparrow} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \downarrow (\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \uparrow (\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \downarrow (\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \uparrow (\vec{r}_2 - \vec{r}_b) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a) \downarrow (\vec{r}_1) \phi_{1s}^H(\vec{r}_2 - \vec{r}_b) \uparrow (\vec{r}_2) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b) \uparrow (\vec{r}_1) \phi_{1s}^H(\vec{r}_2 - \vec{r}_a) \downarrow (\vec{r}_2)).$$

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

Heitler–London theory

Antisymmetric wave function



$$\Psi_{\uparrow\downarrow+\downarrow\uparrow}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_2 - \vec{r}_a)\phi_{1s}^H(\vec{r}_1 - \vec{r}_b)) (\uparrow(\vec{r}_1)\downarrow(\vec{r}_2) + \downarrow(\vec{r}_1)\uparrow(\vec{r}_2)),$$

$$\Psi_{\uparrow\downarrow-\downarrow\uparrow}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) + \phi_{1s}^H(\vec{r}_2 - \vec{r}_a)\phi_{1s}^H(\vec{r}_1 - \vec{r}_b)) (\uparrow(\vec{r}_1)\downarrow(\vec{r}_2) - \downarrow(\vec{r}_1)\uparrow(\vec{r}_2)).$$



Symmetric wave function

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

Molecular orbital:

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+ \uparrow(\vec{r}_1) & \psi_+ \downarrow(\vec{r}_1) \\ \psi_+ \uparrow(\vec{r}_2) & \psi_+ \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{2\sqrt{2}} (\phi_{1s}(\vec{r}_1 - \vec{r}_A) + \phi_{1s}(\vec{r}_1 - \vec{r}_B)) (\phi_{1s}(\vec{r}_2 - \vec{r}_A) + \phi_{1s}(\vec{r}_2 - \vec{r}_B)) (\uparrow\downarrow - \downarrow\uparrow).$$

Homonuclear diatomic molecules

$\text{H}_2, \text{N}_2, \text{O}_2, \dots$

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

All homonuclear diatomic molecules use the molecular orbitals of H_2 .

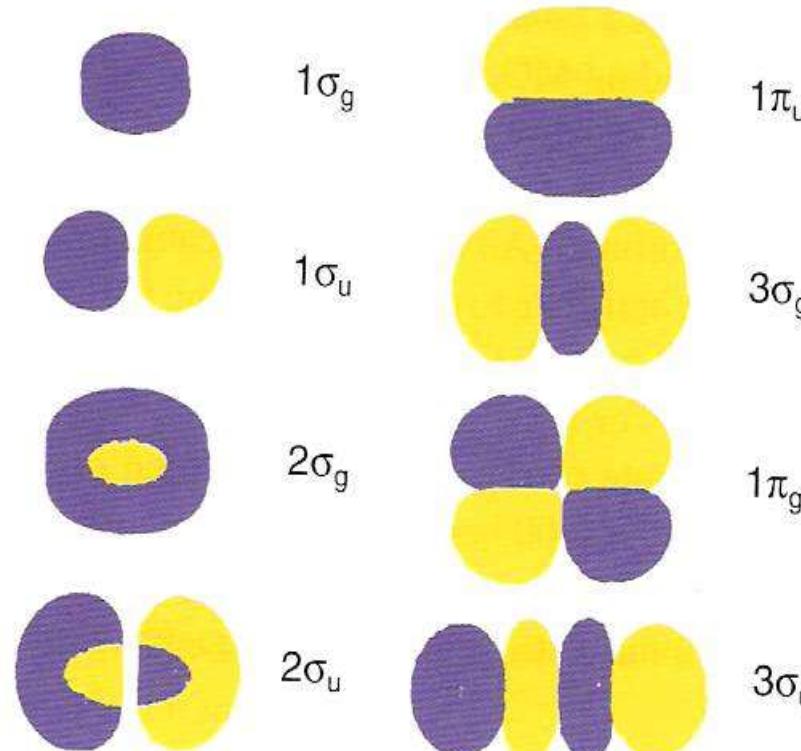
$$\psi_{\text{mo}} = c_1 \phi_{1s,A}^Z + c_2 \phi_{1s,B}^Z + c_3 \phi_{2s,A}^Z + c_4 \phi_{2s,B}^Z + c_5 \phi_{2p_x,A}^Z + c_6 \phi_{2p_x,B}^Z + \dots$$

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

Homonuclear diatomic molecules

All homonuclear diatomic molecules use the molecular orbitals of H₂.

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



$g \rightarrow$ inversion symmetry

from: Blinder, Introduction to Quantum Mechanics

TABLE 11.1 ► Homonuclear Diatomic Molecules

Molecule	Electron Configuration	Bond Order	D_e/eV	$R_e/\text{\AA}$
H_2^+	$1\sigma_g \quad ^2\Sigma_g^+$	0.5	2.79	1.06
H_2	$1\sigma_g^2 \quad ^1\Sigma_g^+$	1	4.75	0.741
He_2	$1\sigma_g^2 1\sigma_u^2 \quad ^1\Sigma_g^+$ $1\sigma_g^2 1\sigma_u 2\sigma_g \quad ^3\Sigma_u^+ \text{ }^b$	0 1	0.0009 ^a 2.6	3.0 1.05
He_2^+	$1\sigma_g^2 1\sigma_u \quad ^2\Sigma_u^+$	0.5	2.5	1.08
Li_2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \quad ^1\Sigma_g^+$	1	1.07	2.67
Be_2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 \quad ^1\Sigma_g^+$	0	0.1	2.5
B_2	$\dots 1\pi_u^2 \quad ^3\Sigma_g^- \text{ }^c$	1	3.0	1.59
C_2	$\dots 1\pi_u^4 \quad ^1\Sigma_g^+$	2	6.3	1.24
N_2	$\dots 1\pi_u^4 3\sigma_g^2 \quad ^1\Sigma_g^+$	3	9.91	1.10
N_2^+	$\dots 1\pi_u^4 3\sigma_g \quad ^2\Sigma_g^+$	2.5	8.85 ^d	1.12
O_2	$\dots 3\sigma_g^2 1\pi_u^4 1\pi_g^2 \quad ^3\Sigma_g^- \text{ }^{c,e}$	2	5.21	1.21
O_2^+	$\dots 3\sigma_g^2 1\pi_u^4 1\pi_g \quad ^2\Pi_g$	2.5	6.78 ^d	1.12
F_2	$\dots 1\pi^4 3\sigma^2 1\pi^4 \quad ^1\Sigma^+$	1	1.66	1.11

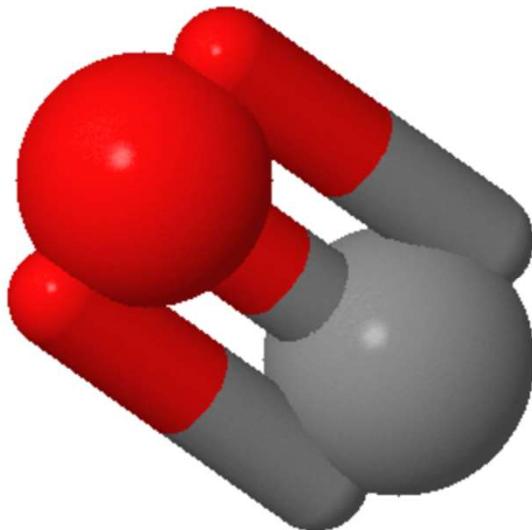
number of electron pairs shared

Bond
Order

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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.

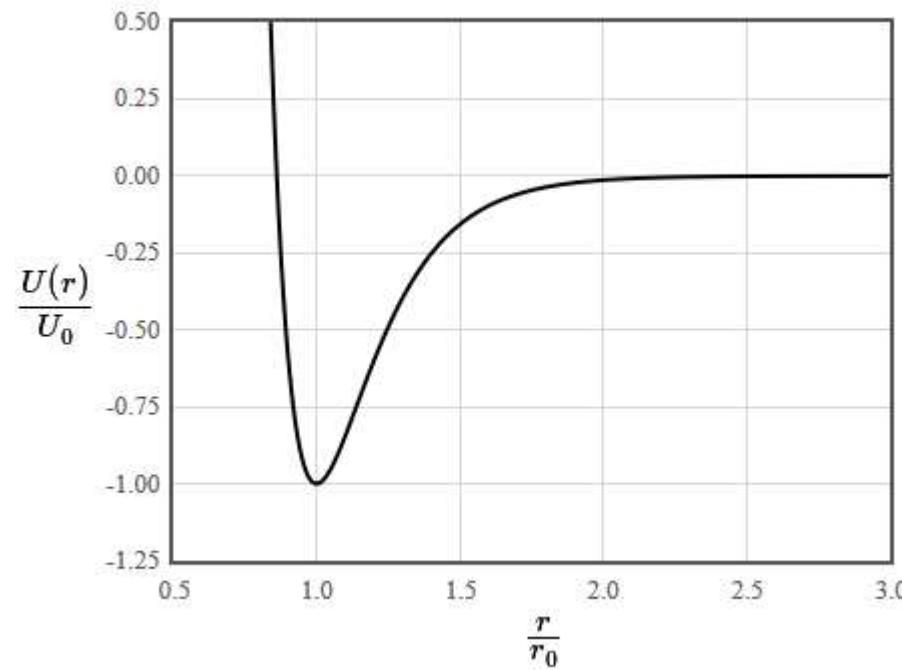


Model: [Ball and Stick](#) [Spacefill](#)

JSmol

Bond potentials

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



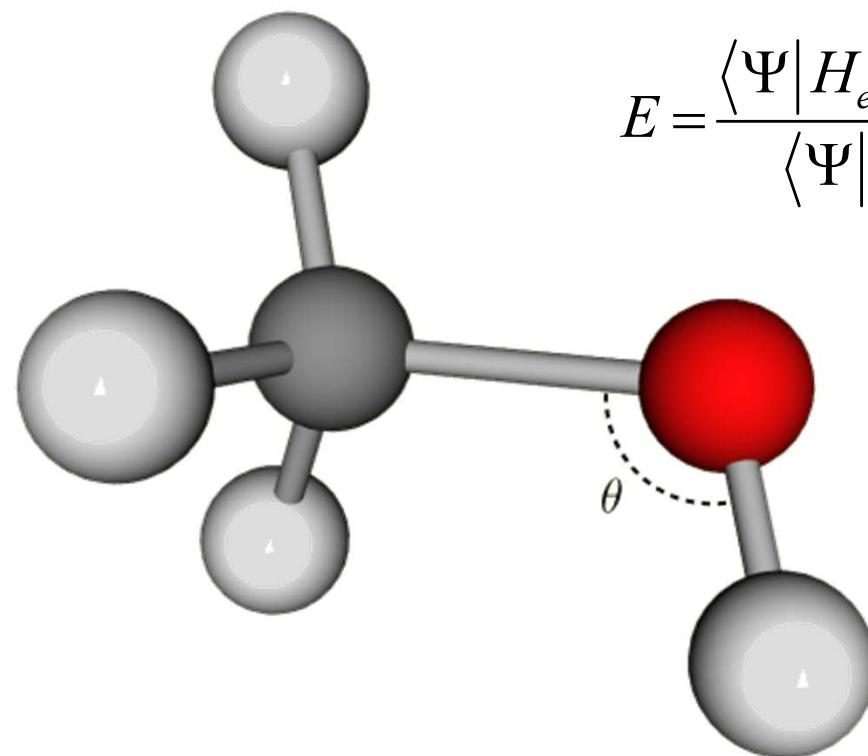
Calculate the energies for different atomic distances.
The minimum yields the bond length and bond strength.

Bondlength (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

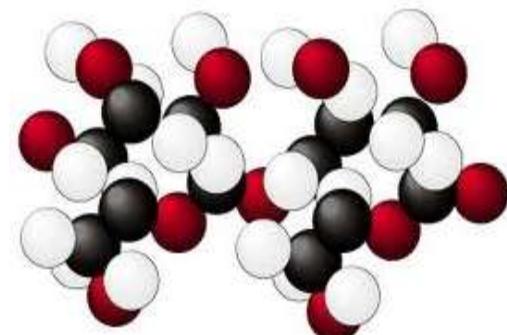
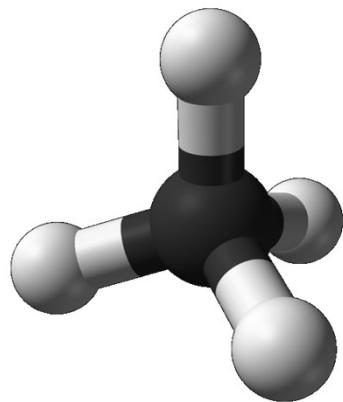
Bond angles

Find the angle that minimizes the energy.

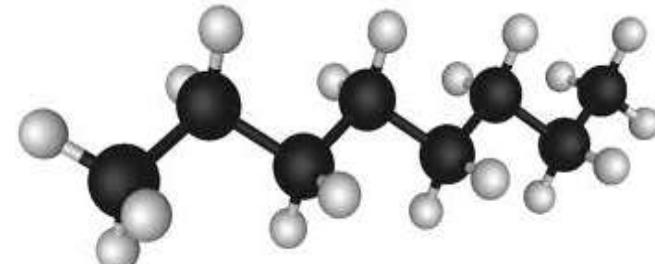
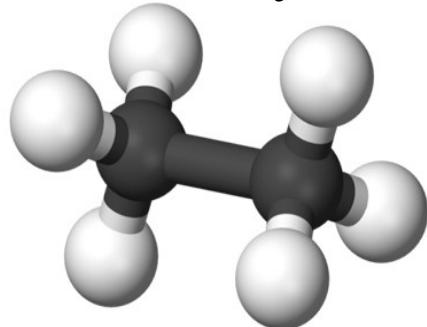
$$E = \frac{\langle \Psi | H_{elec} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$



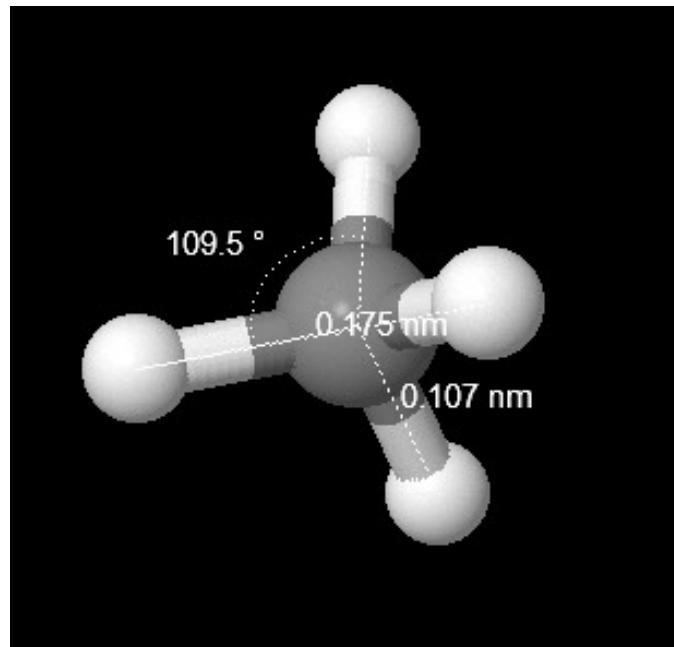
Shape of a molecule



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



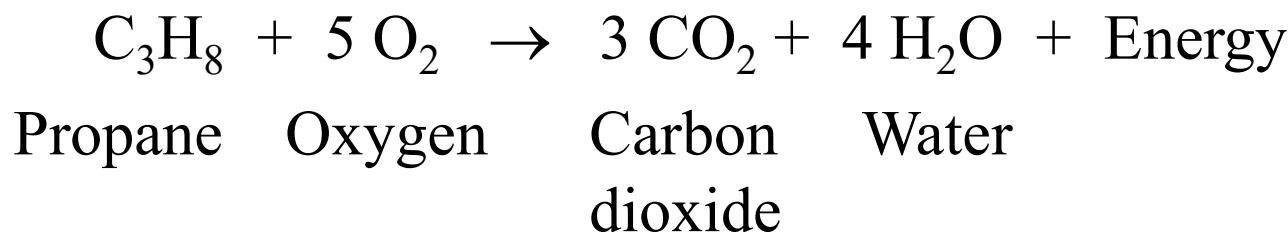
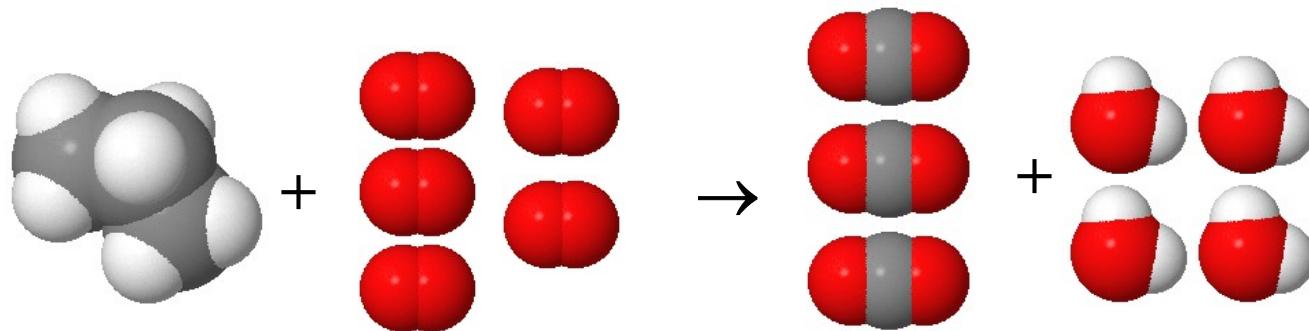
Shape of a molecule



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

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

Chemical reactions

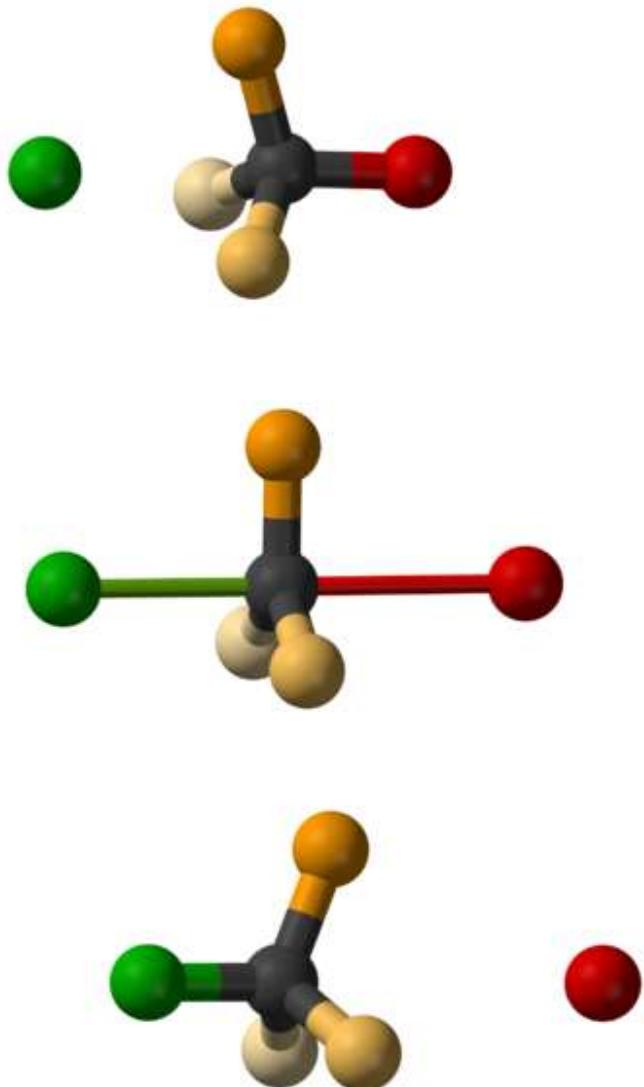


It is possible to calculate if the reaction is endothermic or exothermic.

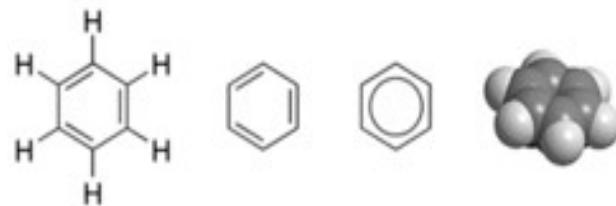
$$E = \frac{\langle \Psi | H_{elec} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Chemical reactions

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



Benzene



42 electrons

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

36 relevant atomic orbitals

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

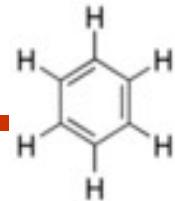
Benzene

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

42 electrons
36 relevant atomic orbitals

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

Benzene



0

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 T^2 have the same eigenvectors

Translation operator

$$T^N = I$$

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

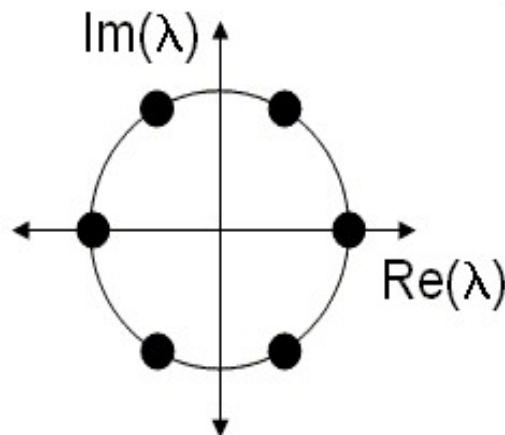
$$T^{-1} \vec{u} = T^{N-1} \vec{u} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix} = \begin{bmatrix}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

Eigen values of the translation operator

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

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

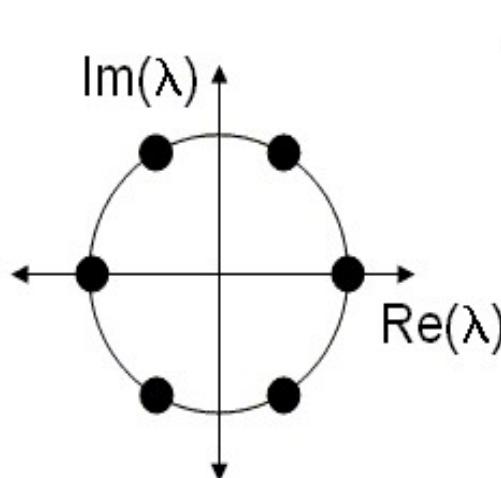
$$\lambda^N = 1$$



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

Eigen vectors of the translation operator

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



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

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

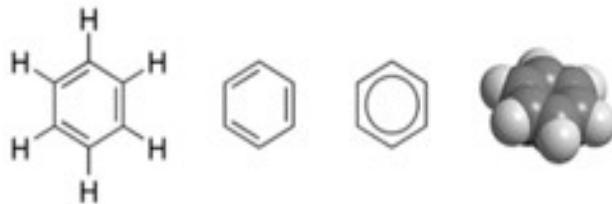
Benzene



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

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

Benzene



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

$$e^{i\pi j/3} + e^{-i\pi j/3} = 2 \cos\left(\frac{\pi j}{3}\right) \quad j=1, 2, \dots, N$$

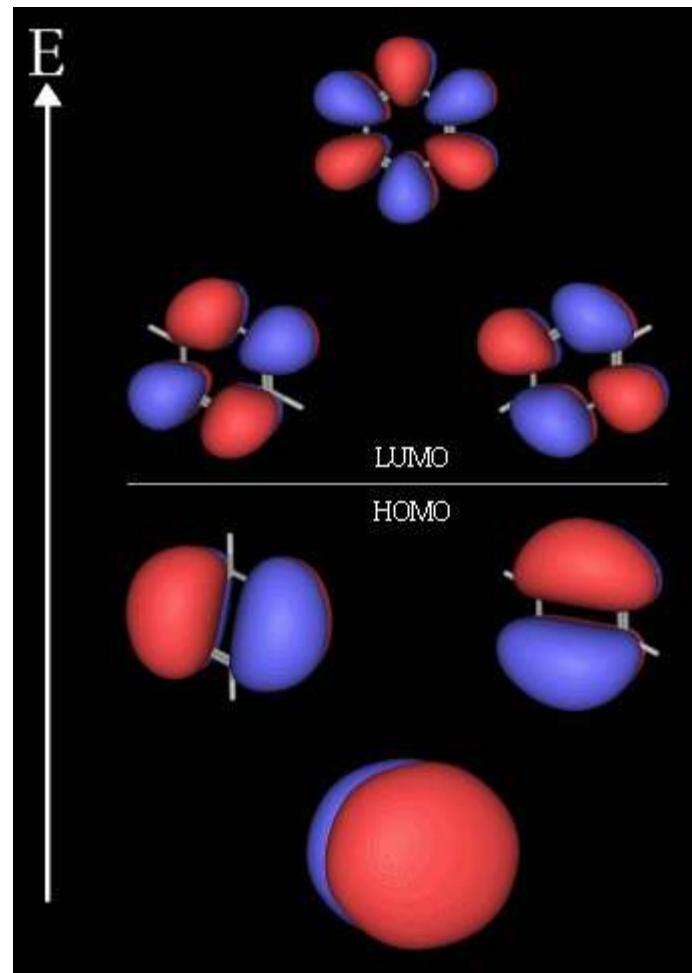
Benzene

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

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

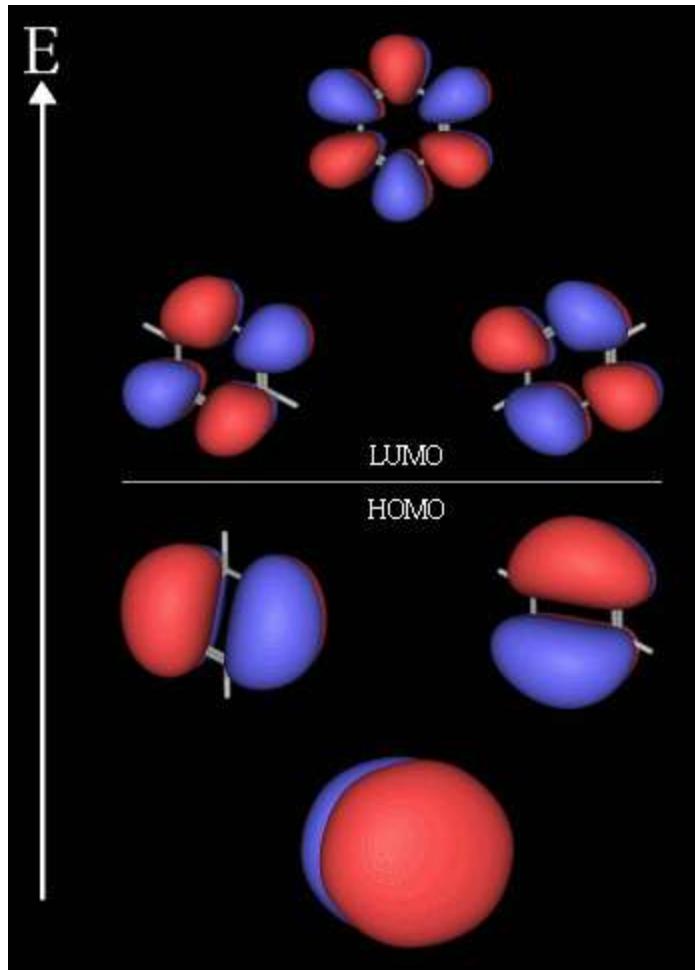
$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{\pi j}{3}\right)}{1 + 2S_{12} \cos\left(\frac{\pi j}{3}\right)}$$

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

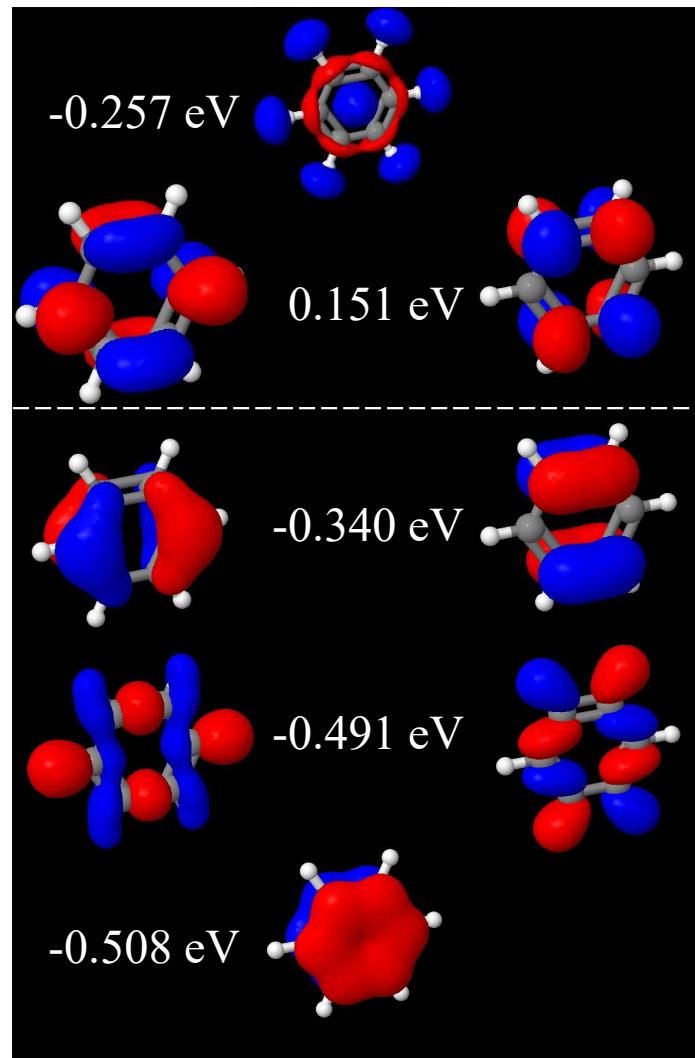


Molecular orbitals benzene

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

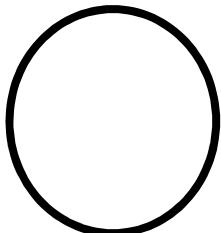
The Roothaan equations for a conjugated ring of N atoms have the form,

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

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

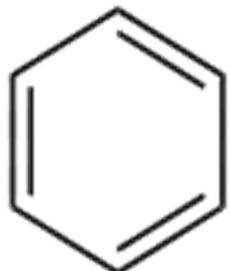
$$\psi_{\text{mo},j} = \frac{1}{\sqrt{N}} \sum_{n=1}^N \exp\left(\frac{i2\pi nj}{N}\right) \phi_{2pz}^C(\vec{r} - \vec{r}_n) \quad j = 1, 2, \dots, N.$$

Particles confined to a ring



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

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

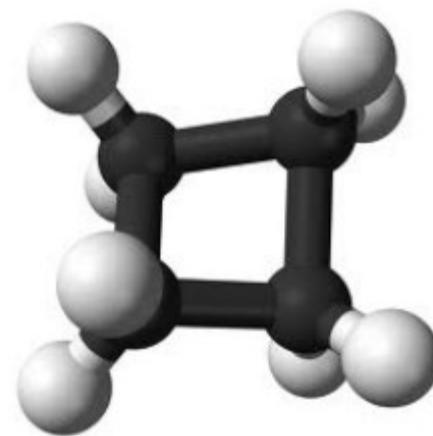
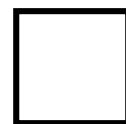


$$E_n = \frac{\hbar^2 n^2}{2mR^2}$$

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

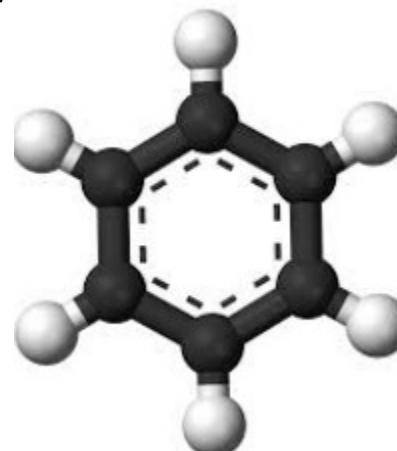
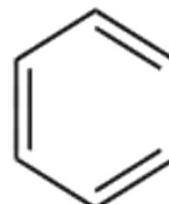
Particles confined to a ring

cyclobutane



$$4n + 2$$

benzene



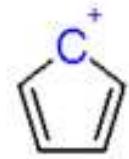
Antiaromaticity

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.

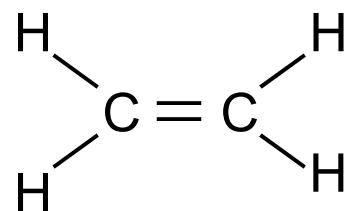


Radicals are electrically neutral but chemically reactive.

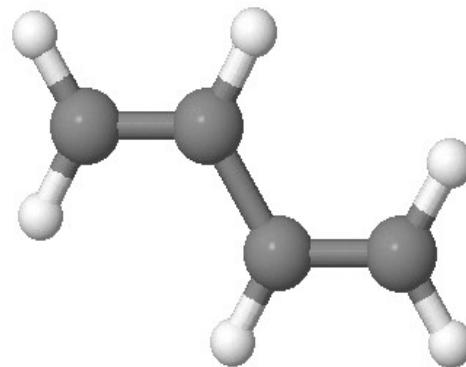
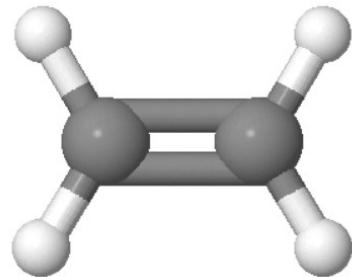
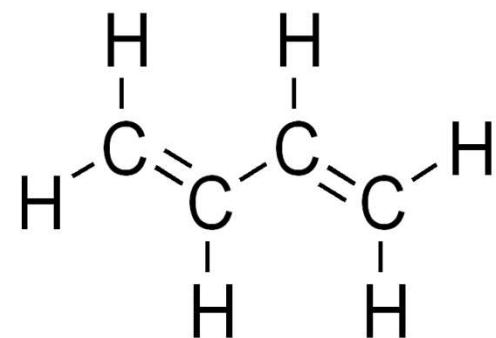


Linear chains

ethene



butadiene



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

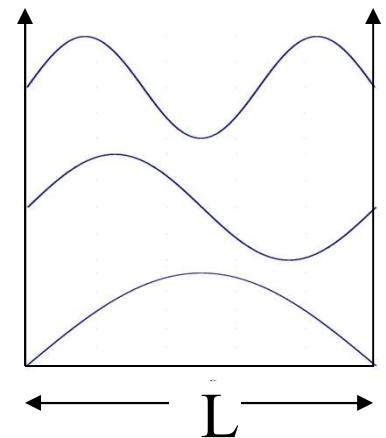
Linear chains

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

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

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

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



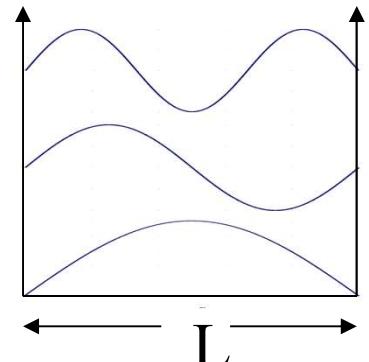
Molecular orbitals of a conjugated chain

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

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

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

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

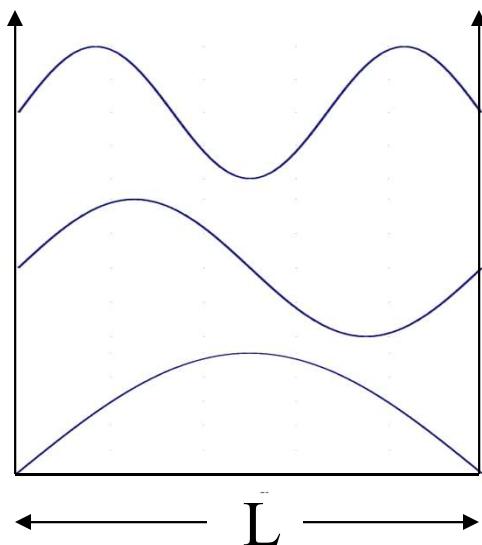


Particles confined to a line

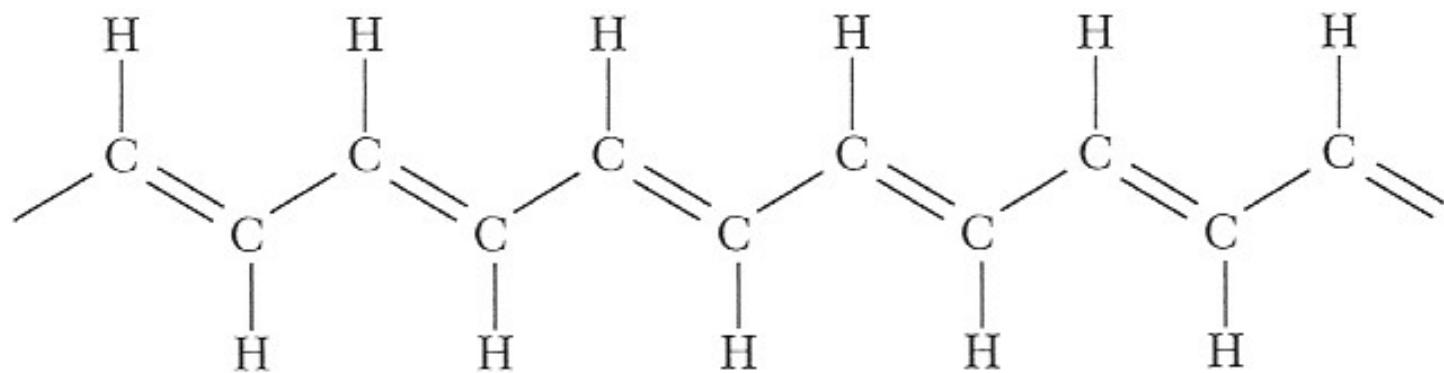
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$$

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

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



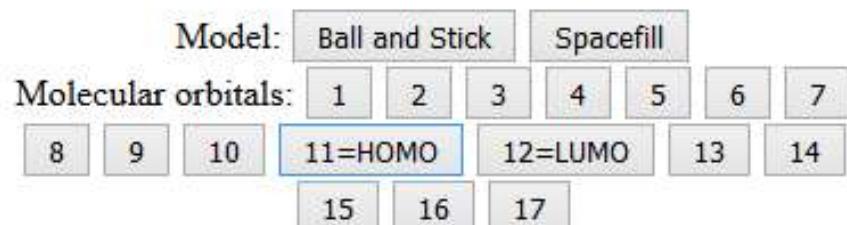
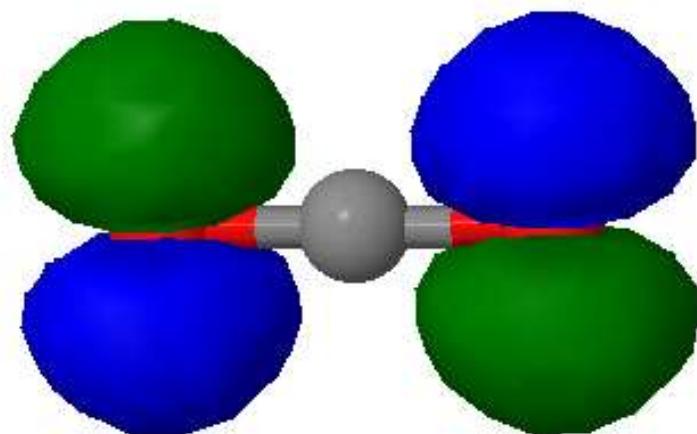
Polyacetylene



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?



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. There is both open source and commercial software. Most of them are large, often containing several separate programs, and have developed over many years.

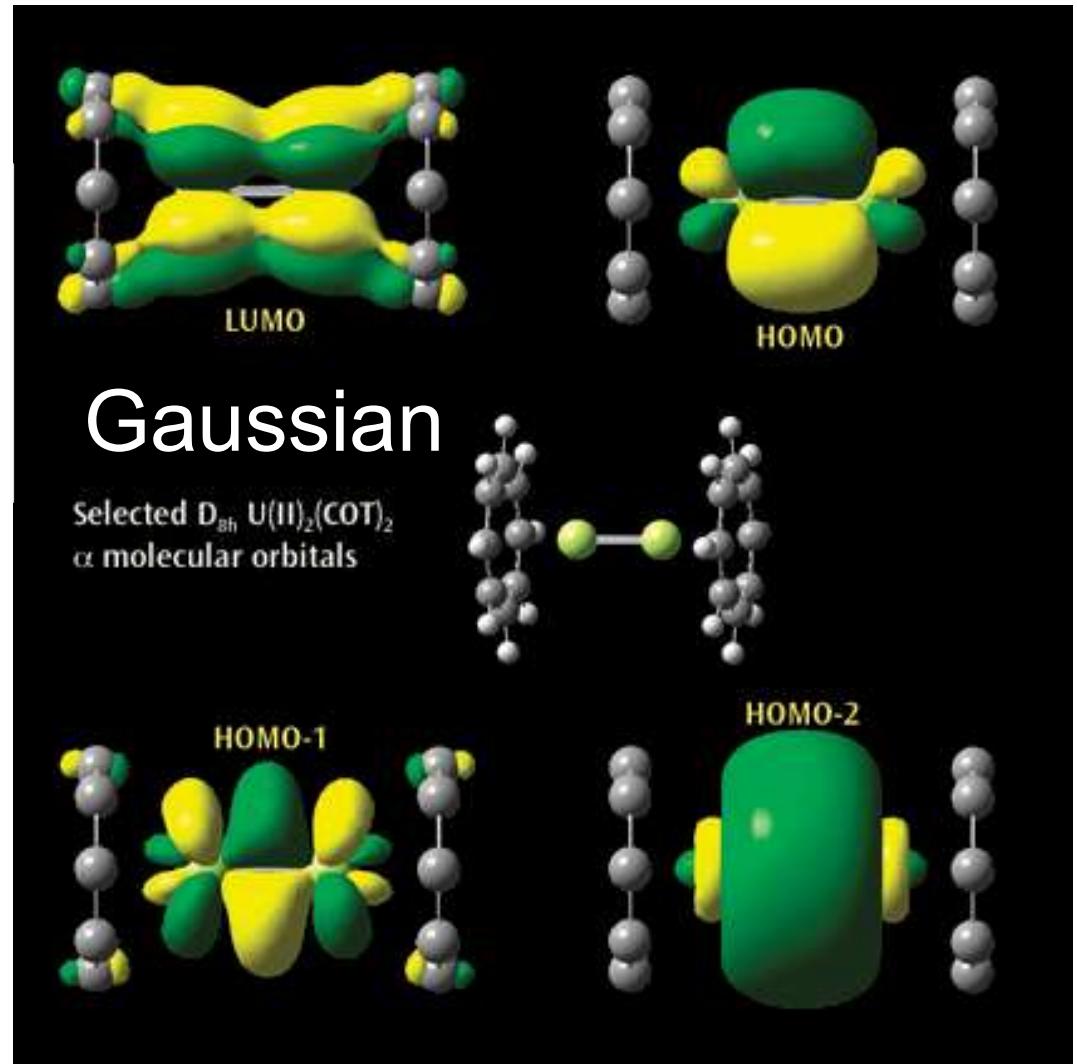
The following table illustrates the capabilities of the most versatile software packages that show an entry in two or more columns of the table.

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	



pyscf

<https://pyscf.org/index.html>



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