

3. Molecules

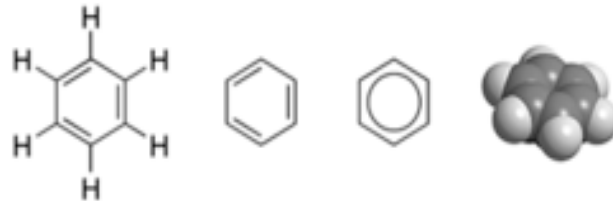
March 13, 2018

The full Hamiltonian of a molecule

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

Everything you can know about the molecule is contained in the Hamiltonian.

This explains life, the universe, and everything!



Born Oppenheimer approximation

Fix the positions of the nuclei and consider the many electron Hamiltonian.

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

This is still too difficult. Neglect the electron-electron interactions.

Separation of variables (Trennung der Veränderlichen)

The Schrödinger equation can be solved by the separation of variables if the total Hamiltonian can be written as a sum of Hamiltonians each depending on only one variable.

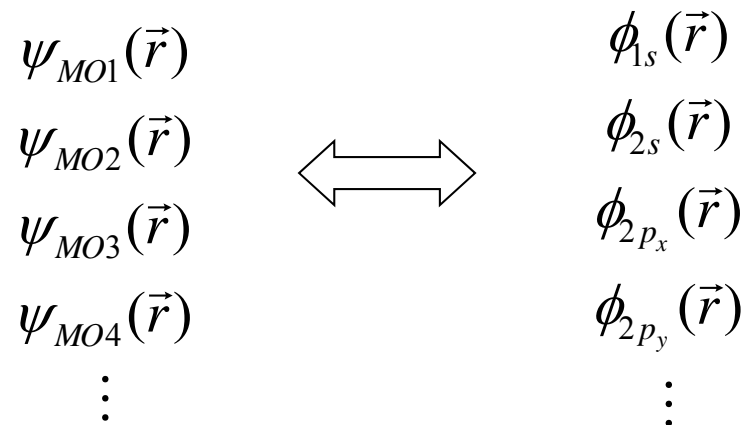
$$H_t(r_1, r_2, \dots, r_n) = H_1(r_1) + H_2(r_2) + \dots + H_n(r_n)$$

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

$$H_{elec_red} = \sum_i \left(\frac{-\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \right) = \sum_i H_{MO}$$

Molecular orbitals

Molecular orbitals of a molecule are like the atomic orbitals of an atom.



You can put two electrons, spin up and spin down, in each molecular orbital.

Molecular orbitals

The first approximation for the many electron wave function of a molecule is an antisymmetrized product of molecular orbitals. The energy of this wave function should be evaluated using the electronic Hamiltonian.

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

Linear Combination of Atomic Orbitals

Look for a solution to the molecular orbital Hamiltonian,

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

of the form,

$$\psi_{\text{mo}} = \sum_n^N c_n \phi_n.$$

Here ϕ_n are atomic orbitals with Z_{eff} .

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.

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

What about spin?

Molecular orbitals of H₂

The time independent Schrödinger equation,

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

Multiply from the left by $\phi_{1s,A}^H$

$$c_1 \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,A}^H \rangle + c_2 \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,B}^H \rangle + \dots = E \left(c_1 \langle \phi_{1s,A}^H | \phi_{1s,A}^H \rangle + c_2 \langle \phi_{1s,A}^H | \phi_{1s,B}^H \rangle + \dots \right)$$

Multiply from the left by $\phi_{1s,B}^H$

$$c_1 \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,A}^H \rangle + c_2 \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,B}^H \rangle + \dots = E \left(c_1 \langle \phi_{1s,B}^H | \phi_{1s,A}^H \rangle + c_2 \langle \phi_{1s,B}^H | \phi_{1s,B}^H \rangle + \dots \right)$$

Two equations with two unknowns: c_1 and c_2

Molecular orbitals of H₂

$$\begin{bmatrix} \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,A}^H \rangle & \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,B}^H \rangle \\ \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,A}^H \rangle & \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,B}^H \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} \langle \phi_{1s,A}^H | \phi_{1s,A}^H \rangle & \langle \phi_{1s,A}^H | \phi_{1s,B}^H \rangle \\ \langle \phi_{1s,B}^H | \phi_{1s,A}^H \rangle & \langle \phi_{1s,B}^H | \phi_{1s,B}^H \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

Roothaan equations: $\begin{bmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{12}^* & S_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$

Hamiltonian matrix

Overlap matrix

The eigenvectors of both matrices are

$$\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

Molecular orbitals of H₂

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} \\ S_{12} & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$H_{11} + H_{12} = E_+ (1 + S_{12})$$

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} 1 \\ -1 \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} \\ S_{12} & 1 \end{bmatrix} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

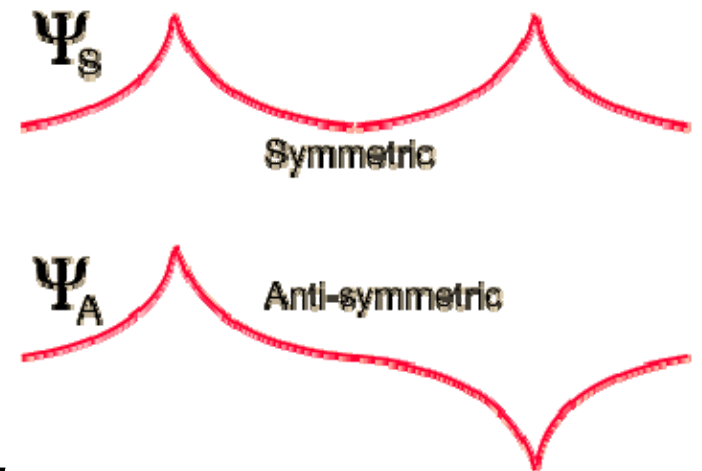
$$H_{11} - H_{12} = E_- (1 - S_{12})$$

Molecular orbitals of H₂

The eigen values and eigen functions are:

$$E_+ = \frac{H_{11} + H_{12}}{1 + S_{12}}, \quad E_- = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$\psi_{\pm}(\vec{r}) = \frac{1}{\sqrt{2}} \left(\phi_{1sA}^H(\vec{r}) \pm \phi_{1sB}^H(\vec{r}) \right)$$



Both H_{AA} and H_{AB} are negative $E_+ < E_-$

Molecular orbitals of H₂

In the ground state, both electrons occupy the lower energy symmetric orbital (bonding orbital).

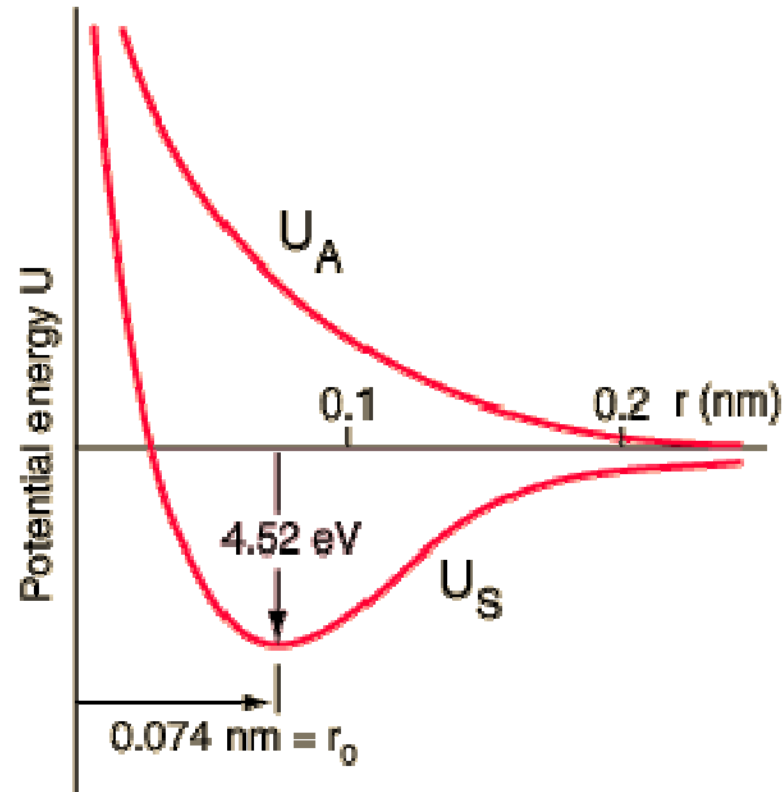
$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+ \uparrow(\vec{r}_1) & \psi_+ \downarrow(\vec{r}_1) \\ \psi_+ \uparrow(\vec{r}_2) & \psi_+ \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \psi_+(\vec{r}_1) \psi_+(\vec{r}_2) (\uparrow\downarrow - \downarrow\uparrow)$$

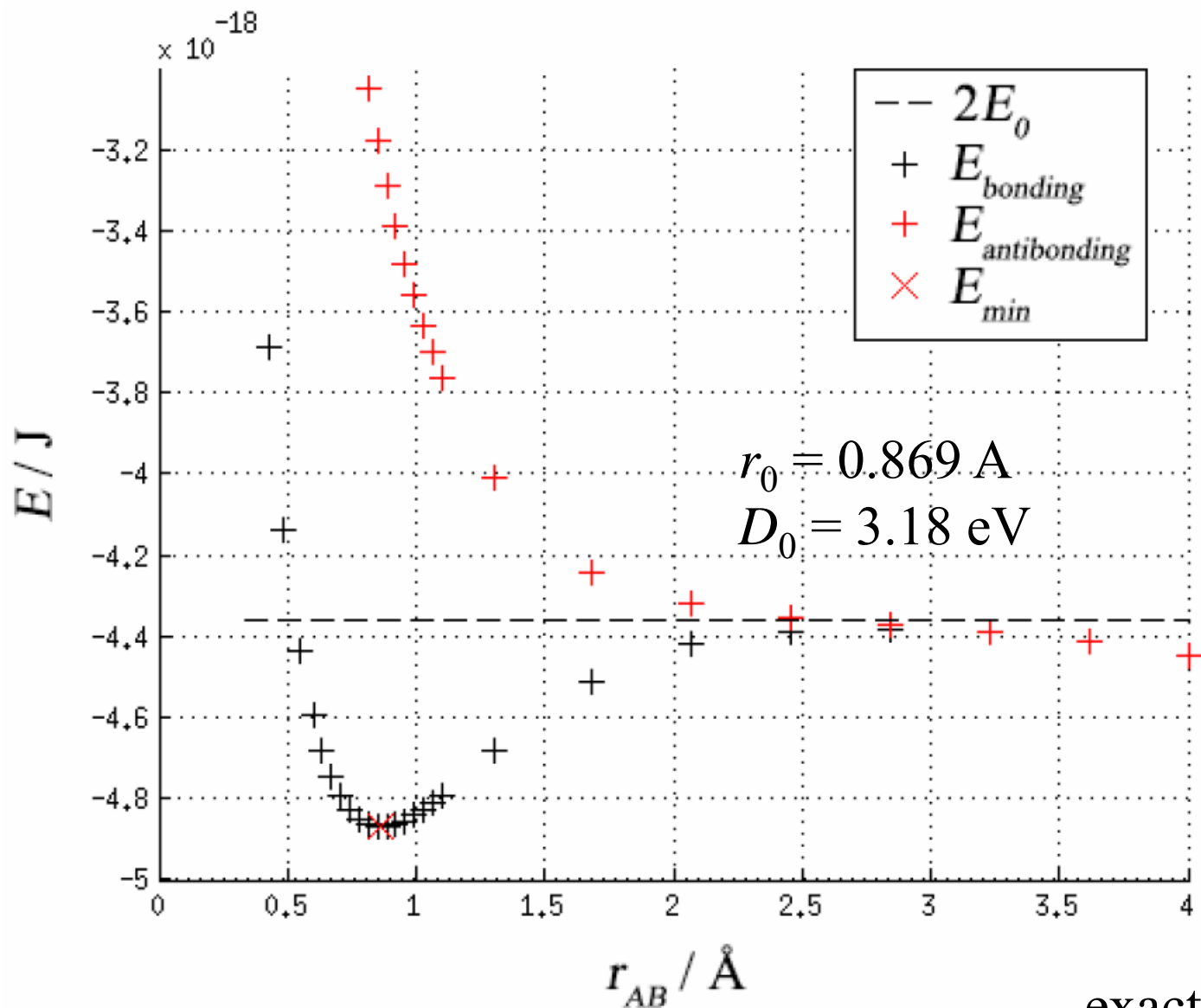
$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{2\sqrt{2}} \left(\phi_{1sA}^H(\vec{r}_1) \phi_{1sA}^H(\vec{r}_2) + \phi_{1sA}^H(\vec{r}_1) \phi_{1sB}^H(\vec{r}_2) + \phi_{1sA}^H(\vec{r}_2) \phi_{1sB}^H(\vec{r}_1) + \phi_{1sB}^H(\vec{r}_1) \phi_{1sB}^H(\vec{r}_2) \right) (\uparrow\downarrow - \downarrow\uparrow)$$

Use this wave function including the electron-electron interaction to calculate the bond potential.

Student project: Draw the Bond potential of H₂

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





exact values
 $r_0 = 0.74 \text{ \AA}$
 $D_0 = 4.52 \text{ eV}$

Homonuclear diatomic molecules

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

All homonuclear diatomic molecules use the molecular orbitals of H_2 .

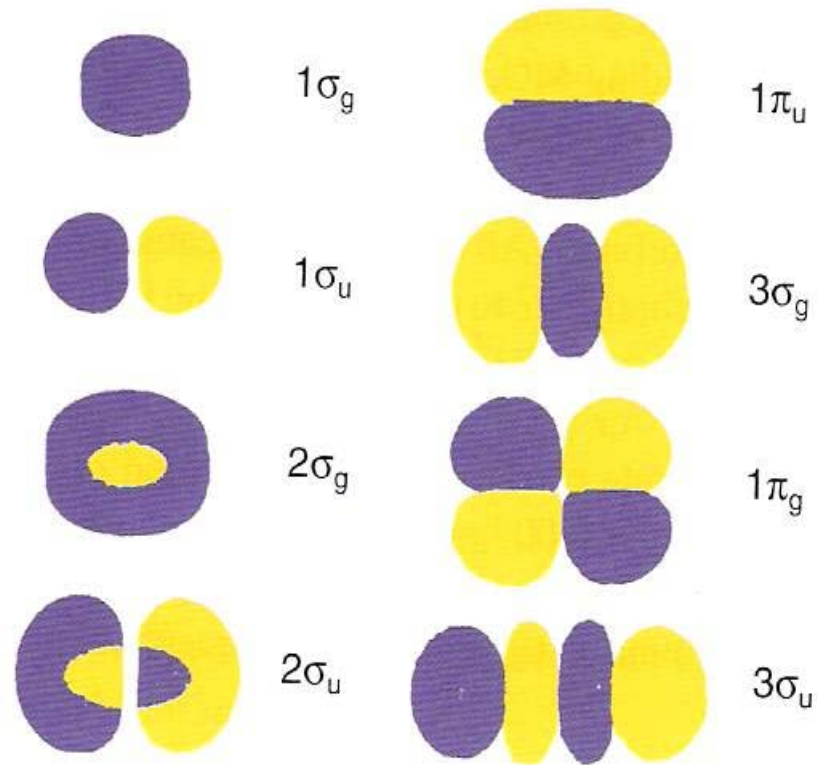
$$\psi_{mo} = c_1 \phi_{1s,A}^Z + c_2 \phi_{1s,B}^Z + c_3 \phi_{2s,A}^Z + c_4 \phi_{2s,B}^Z + c_5 \phi_{2p_x,A}^Z + c_6 \phi_{2p_x,B}^Z + \dots$$

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 H_2 .

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



$g \rightarrow$ inversion symmetry

from: Blinder, Introduction to Quantum Mechanics

number of electron pairs shared

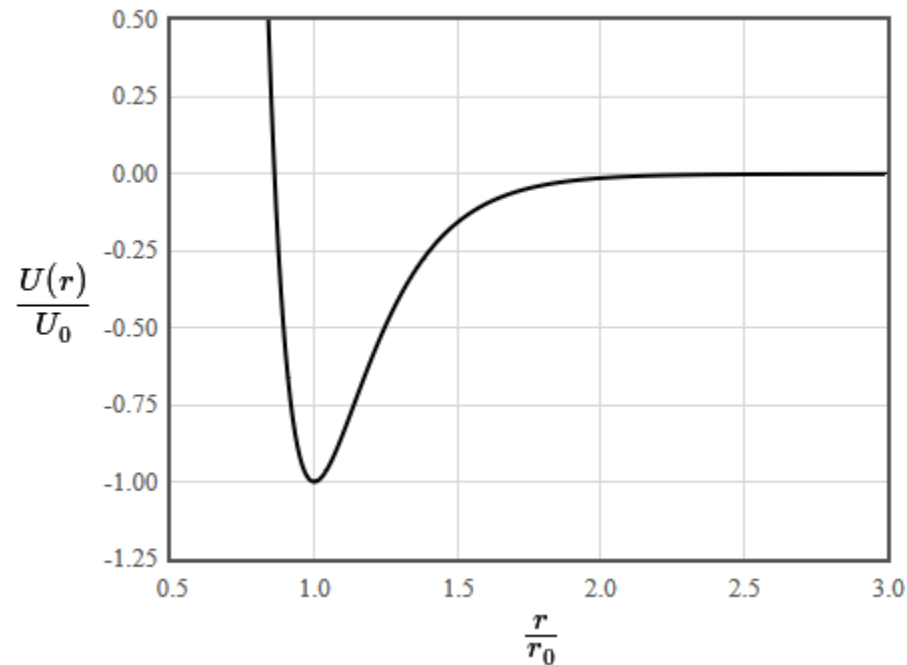
TABLE 11.1 ► **Homonuclear Diatomic Molecules**

Molecule	Electron Configuration	Bond Order	D_e/eV	$R_{ej}/\text{\AA}$
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	$\dots 1\pi_u^2 \ 3\Sigma_g^- \ c$	1	3.0	1.59
C_2	$\dots 1\pi_u^4 \ 1\Sigma_g^+$	2	6.3	1.24
N_2	$\dots 1\pi_u^4 3\sigma_g^2 \ 1\Sigma_g^+$	3	9.91	1.10
N_2^+	$\dots 1\pi_u^4 3\sigma_g \ 2\Sigma_g^+$	2.5	8.85 ^d	1.12
O_2	$\dots 3\sigma_g^2 1\pi_u^4 1\pi_g^2 \ 3\Sigma_g^- \ c,e$	2	5.21	1.21
O_2^+	$\dots 3\sigma_g^2 1\pi_u^4 1\pi_g \ 2\Pi_g$	2.5	6.78 ^d	1.12
F_2	$\dots 1\pi_u^4 3\sigma_g^2 1\pi_g^4 \ 1\Sigma_g^+$	1	1.66	1.41

from: Blinder, Introduction to Quantum Mechanics

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.

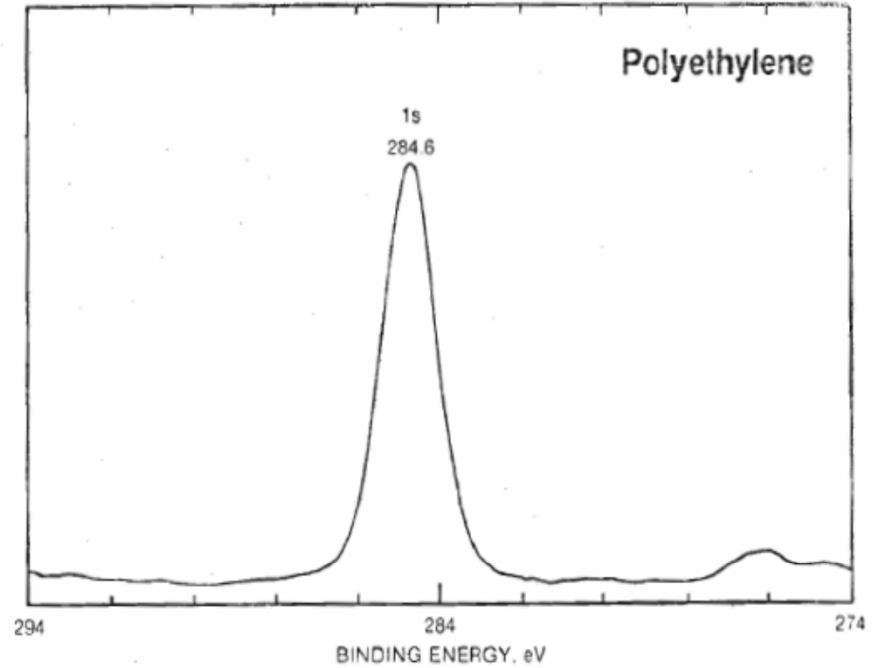
Bondlength (nm) and bond energy (eV)					
Bond	Length	Energy	Bond	Length	Energy
H--H	0.074	4.52	H--C	0.109	4.28
C--C	0.154	3.61	H--N	0.101	4.05
C=C	0.134	6.36	H--F	0.092	5.89
C≡C	0.120	8.70	H--O	0.096	3.79
C--O	0.143	3.73	H--Cl	0.127	4.48
C--S	0.182	2.82	H--Br	0.141	3.79
C--F	0.135	5.06	H--I	0.161	3.09
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

XPS

Carbon, C Atomic Number 6

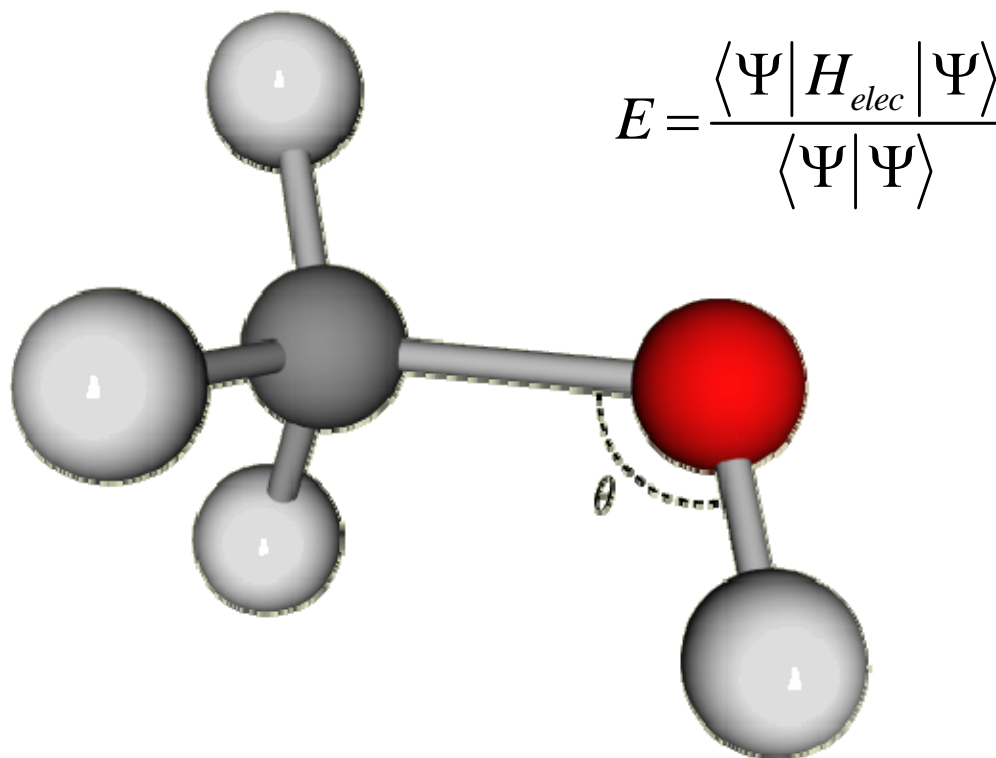
HANDBOOK OF X-RAY PHOTOELECTRON SPECTROSCOPY

COMPOUND	1s BINDING ENERGY, eV					REF.
	280	284	288	292	296	
HfC						RH1
TiC						RH1
WC						RH1
C (graphite)						HJG
(CH ₂) _n						Φ
Mn(C ₅ H ₅) ₂						BCD
SnPh ₄						BAL
MeCH ₂ NH ₂						GHH
Cr(C ₆ H ₆) ₂						PFD
MeCH ₂ Cl						GHH
MeCH ₂ OH						GHH
MeCH ₂ OEt						GHH
MeCH ₂ OOCMe						GHH
CS ₂						GHH
Fe(CO) ₅						BC1
Me ₂ CO						GHH
(NH ₂) ₂ CO						GHH
C ₅ F ₆						GHH
MeCOONa						GHH
MeCOOEt						GHH
MeCOOH						GHH
Na ₂ CO ₃						GHH
NaHCO ₃						GHH
CO						BC1
CO ₂						GHH
(CHFCH ₂) _n						CFK
(CHFCHF) _n						CFK
(CHFCH ₂) _n						CFK
(CF ₂ CH ₂) _n						CFK
(CF ₂ CHF) _n						CFK
(CF ₂) _n						CFK
CF ₃ COONa						GHH
CCl ₄						GHH
CF ₃ COMe						GHH
CF ₃ COOEt						GHH

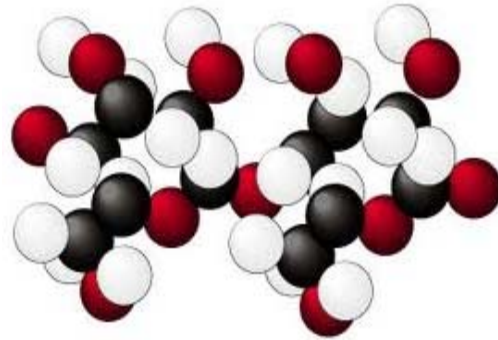
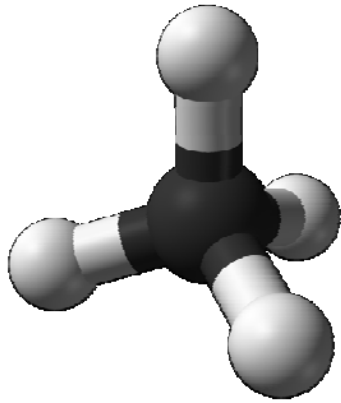


Bond angles

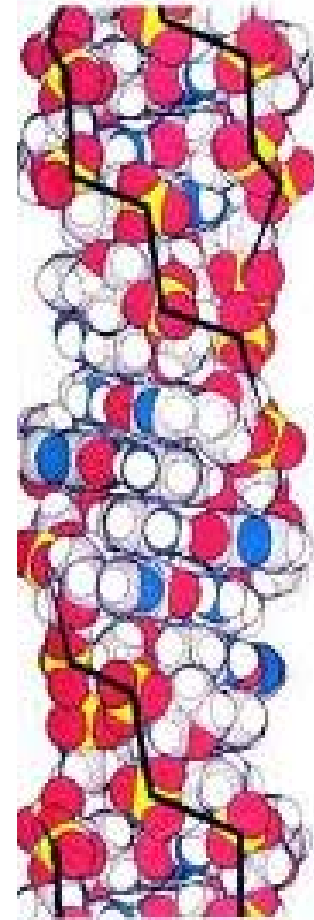
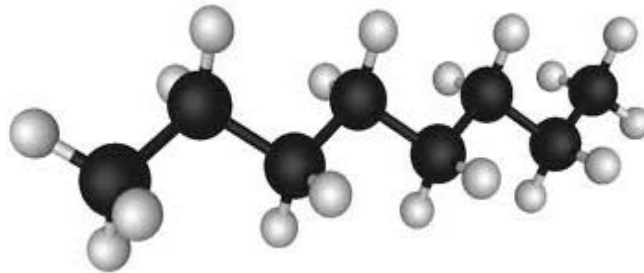
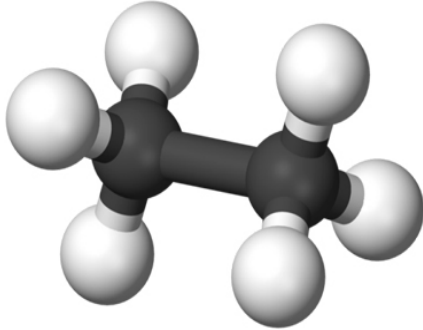
Find the angle that minimizes the energy.



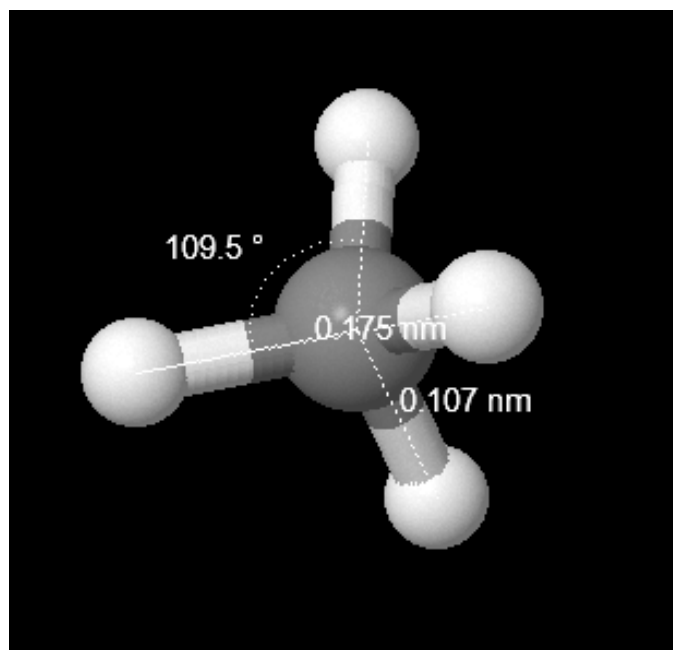
Shape of a molecule



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



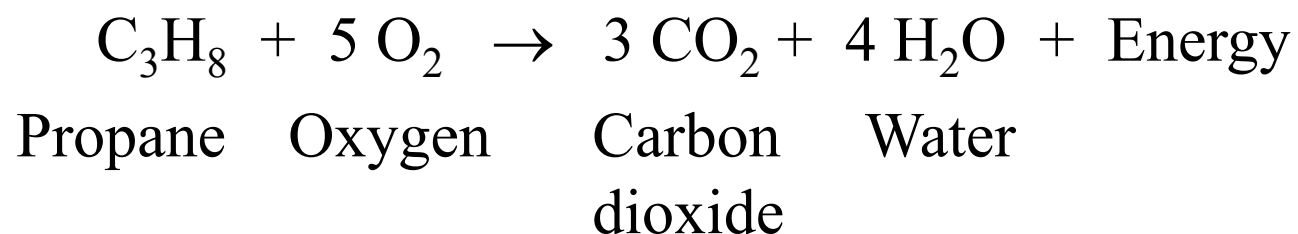
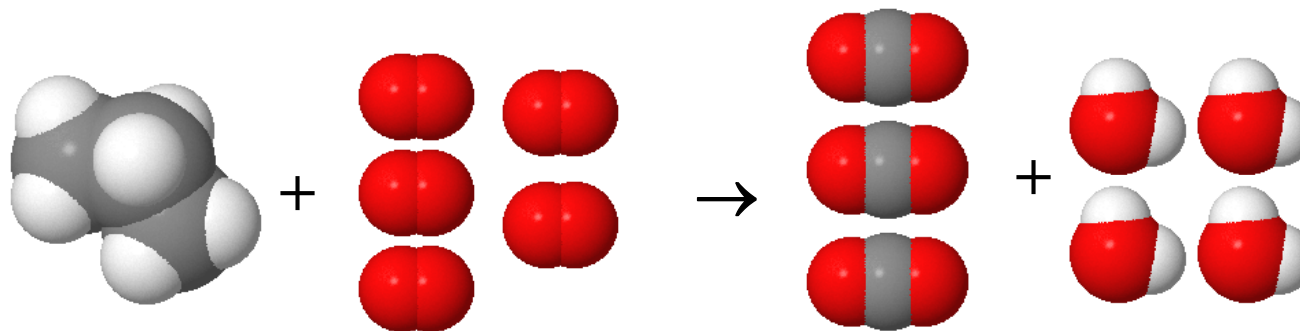
Shape of a molecule



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

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

Chemical reactions

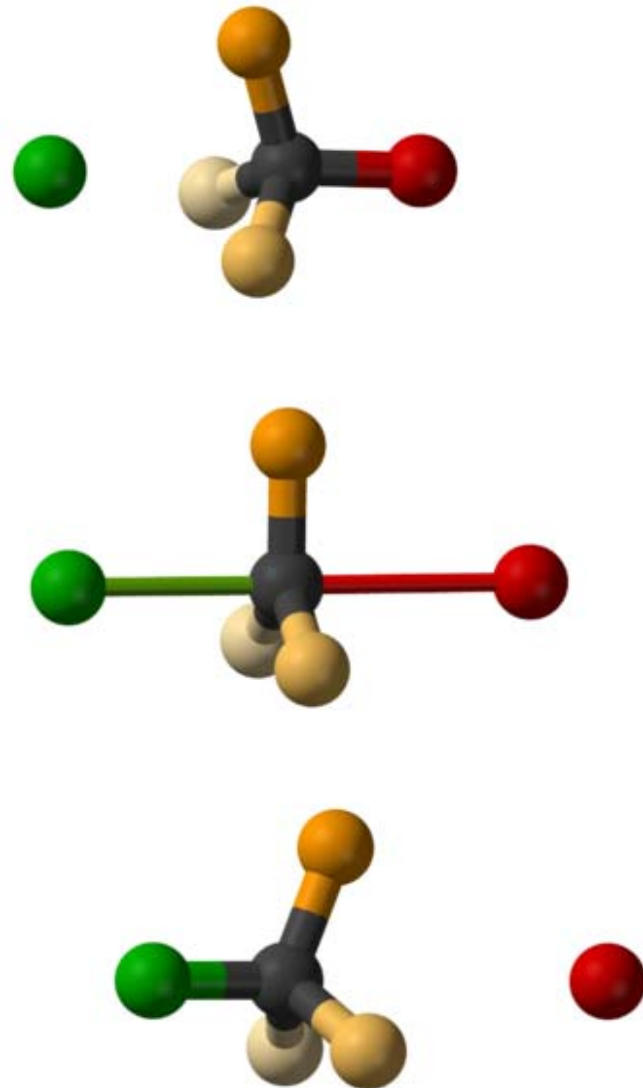


It is possible to calculate if the reaction is endothermic or exothermic.

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

Chemical reactions

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



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

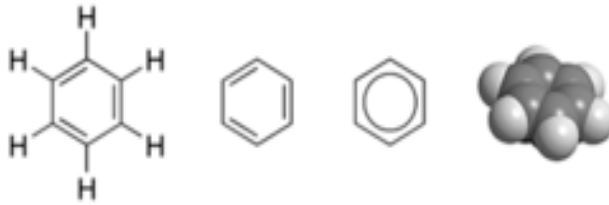
$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

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)

Benzene



Assume the valence molecular orbital is

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

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