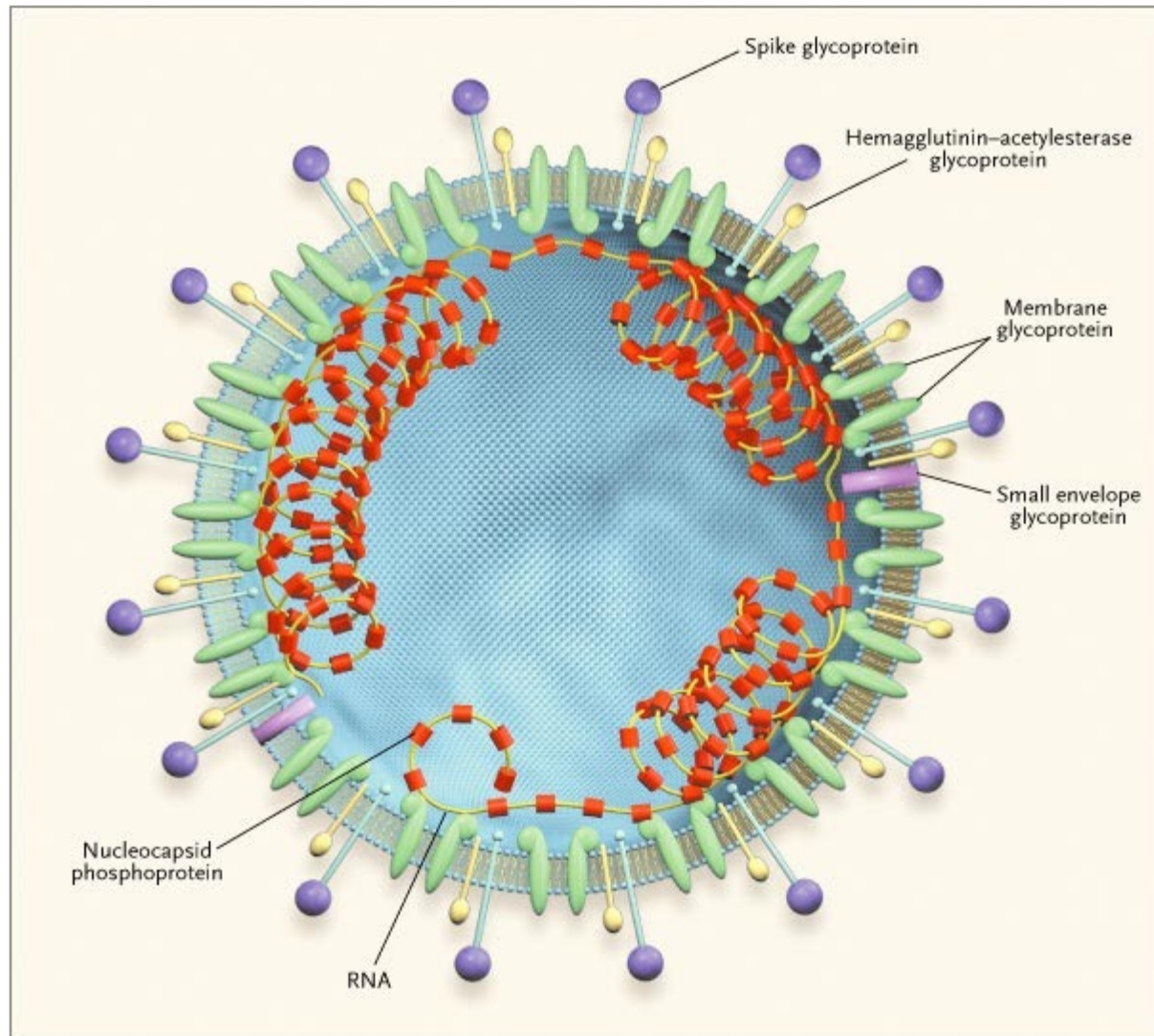# 4. Molecules

Mar. 12, 2020

Structure of the Coronavirus

Review: Molecules

Start with the full Hamiltonian

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

Use the Born-Oppenheimer approximation

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

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

$$H_{MO} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 |r_1 - r_A|}$$

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

Molecular orbitals of the molecular ion H₂⁺

The molecular ion H_2^+ consists of one electron and two protons. The molecular orbital Hamiltonian in this case is,

$$H_{\text{mo}}^{H_2^+} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_B|}, \tag{1}$$
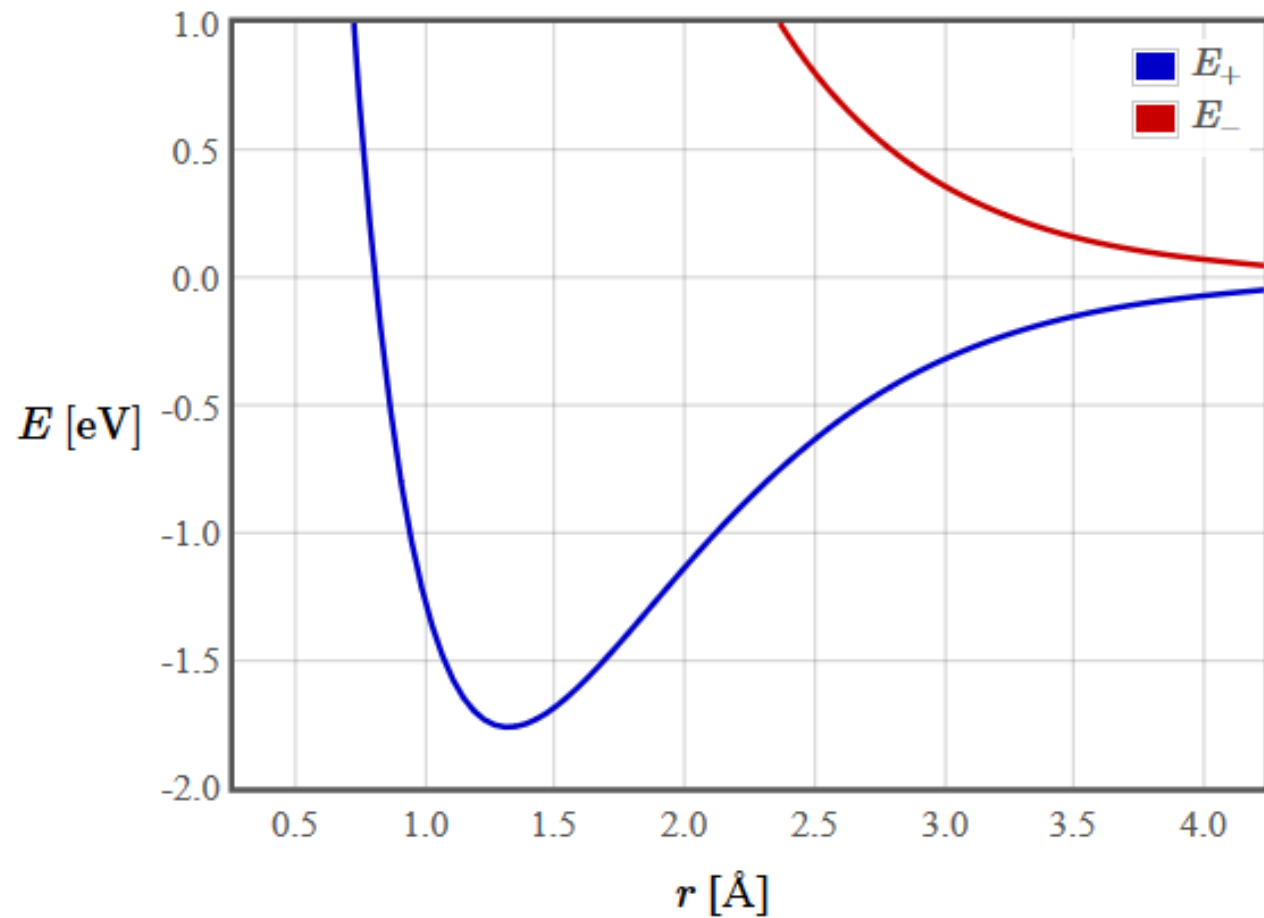
where $\vec{r}_A$ and $\vec{r}_B$ are the positions of the two protons. Consider a linear combination of the two 1s orbitals, $\psi_{\text{mo}} = c_1\phi_{1s}(\vec{r} - \vec{r}_A) + c_2\phi_{1s}(\vec{r} - \vec{r}_B)$. The time independent Schrödinger equation is,

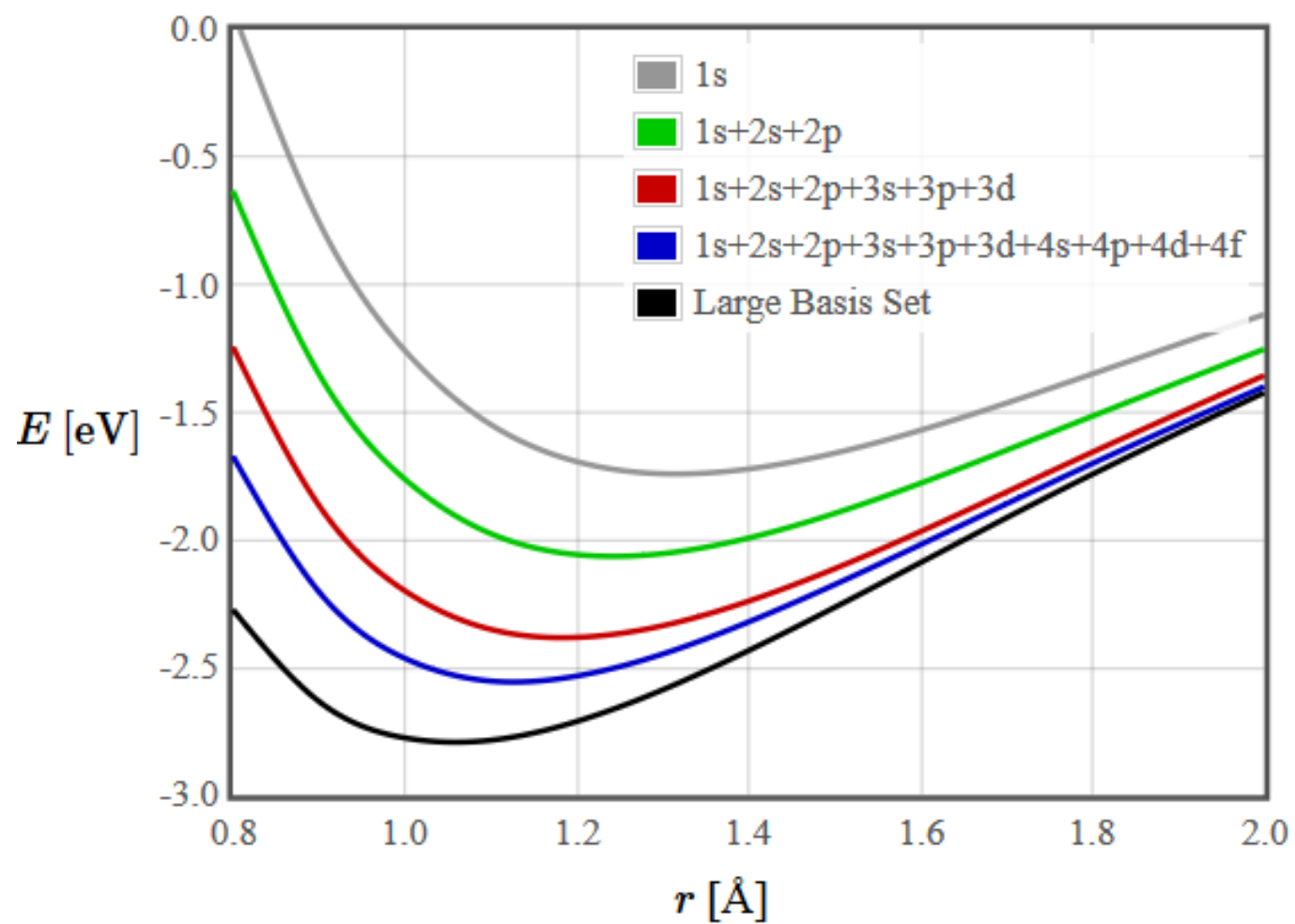$$H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}. \tag{2}$$

http://lampx.tugraz.at/~hadley/ss1/molecules/hueckel/mo_h2_plus.php

Molecular orbitals of H$_2^+$

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

Molecular orbitals of H_2^+

Molecular orbitals of H$_2$

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

$$\Psi\left(\vec{r_1},\vec{r_2}\right) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+ \uparrow(\vec{r_1}) & \psi_+ \downarrow(\vec{r_1}) \\ \psi_+ \uparrow(\vec{r_2}) & \psi_+ \downarrow(\vec{r_2}) \end{vmatrix} = \frac{1}{\sqrt{2}} \psi_+(\vec{r_1})\psi_+(\vec{r_2})\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

$$\Psi\left(\vec{r_1},\vec{r_2}\right) = \frac{1}{2\sqrt{2}}\left(\phi_{1sA}^{H}(\vec{r_1})\phi_{1sA}^{H}(\vec{r_2}) + \phi_{1sA}^{H}(\vec{r_1})\phi_{1sB}^{H}(\vec{r_2}) + \phi_{1sA}^{H}(\vec{r_2})\phi_{1sB}^{H}(\vec{r_1}) + \phi_{1sB}^{H}(\vec{r_1})\phi_{1sB}^{H}(\vec{r_2})\right)\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

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

Homonuclear diatomic molecules

$$H_2, N_2, O_2, ...$$

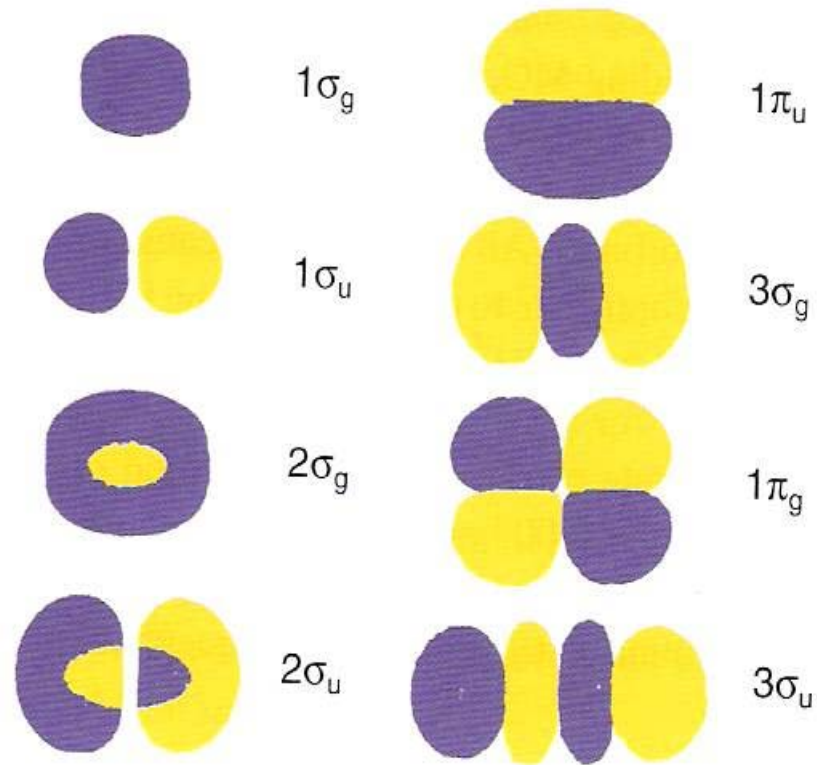All homonuclear diatomic molecules use the molecular orbitals of H_2.

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

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

Homonuclear diatomic molecules

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

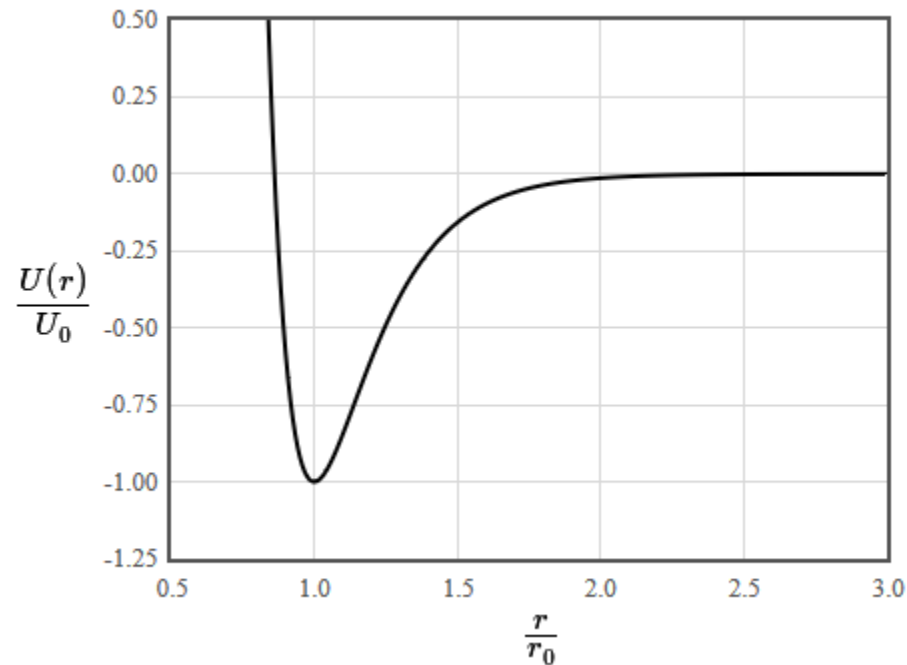number of electron pairs shared

TABLE 11.1 ▶ Homonuclear Diatomic Molecules

Molecule	Electron Configuration	Bond Order	D_e/eV	R_e/Å
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	$1\sigma_g^2 1\sigma_u^2$ $\quad^1\Sigma_g^+$	0	0.0009^a	3.0
	$1\sigma_g^2 1\sigma_u 2\sigma_g$ $\quad^3\Sigma_u^+$ ^{b}	1	2.6	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	$\ldots 1\pi_u^2$ $\quad^3\Sigma_g^-$ ^{c}	1	3.0	1.59
C_2	$\ldots 1\pi_u^4$ $\quad^1\Sigma_g^+$	2	6.3	1.24
N_2	$\ldots 1\pi_u^4 3\sigma_g^2$ $\quad^1\Sigma_g^+$	3	9.91	1.10
N_2^+	$\ldots 1\pi_u^4 3\sigma_g$ $\quad^2\Sigma_g^+$	2.5	8.85 ^{d}	1.12
O_2	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2$ $\quad^3\Sigma_g^-$ ^{c,e}	2	5.21	1.21
O_2^+	$\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g$ $\quad^2\Pi_g$	2.5	6.78 ^{d}	1.12
F_2	$\ldots 1\pi_u^4 3\sigma_g^2 1\pi_g^4$ $\quad^1\Sigma^+$	1	1.66	1.41

Bond potentials

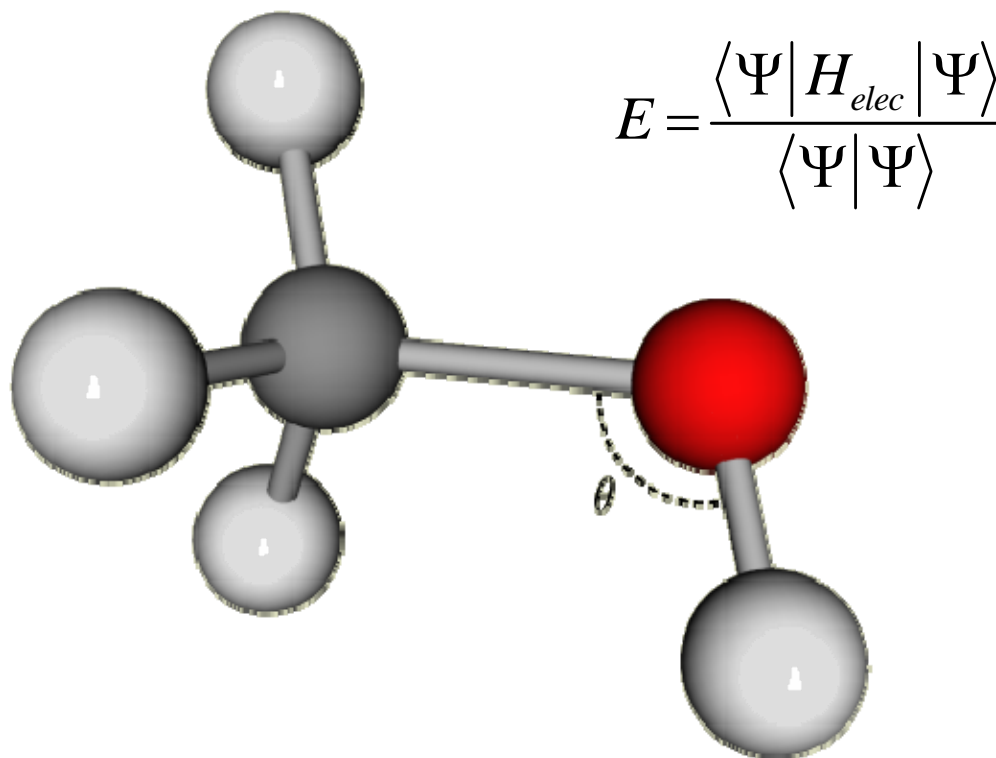$$E = \frac{\langle \Psi | H_{elec} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

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.

$$E = \frac{\langle \Psi | H_{elec} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$
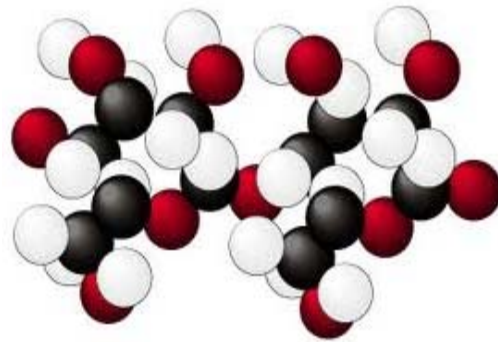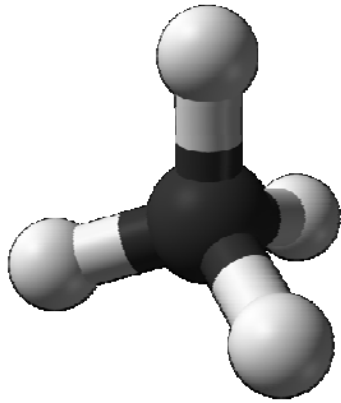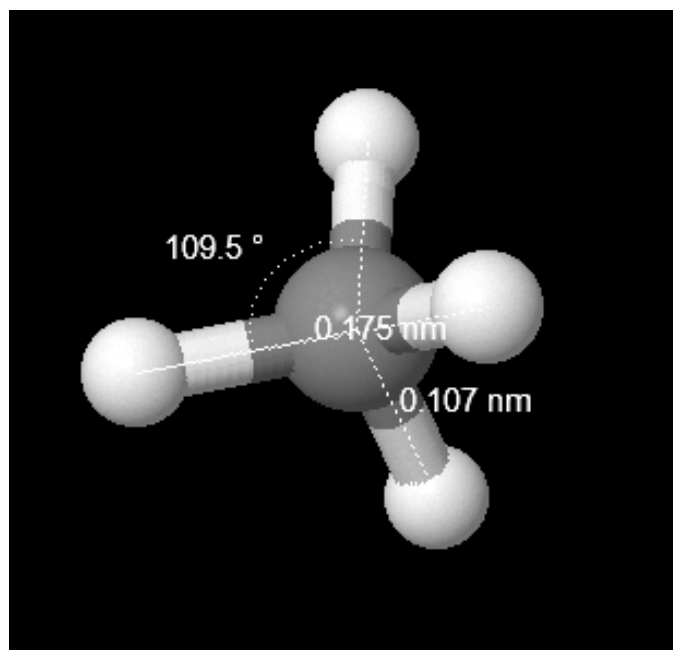
Shape of a molecule

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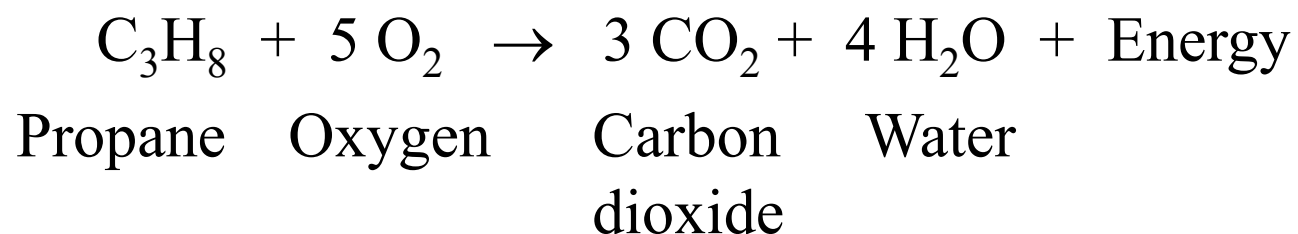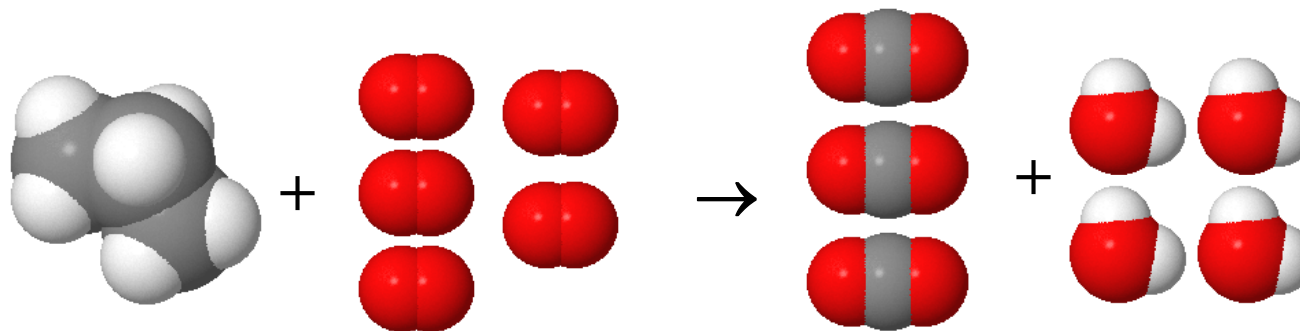
Shape of a molecule

109.5 °

0.175 nm

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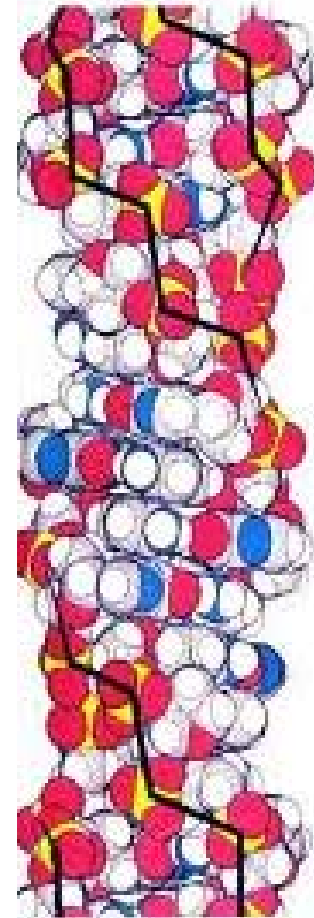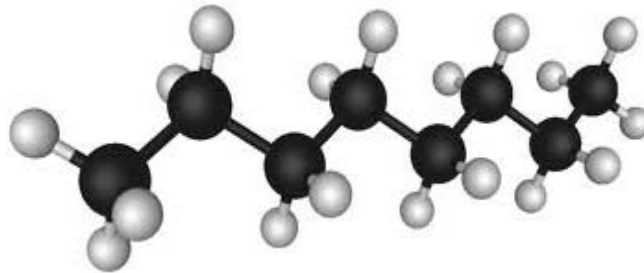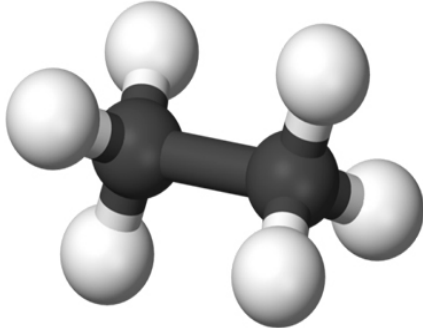
In Jmol, double click to start and stop a measurement.

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   Water
dioxide

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.