

# Orbital approximation

- Assign the electrons to an atomic orbital and a spin
- Construct an antisymmetrized wave function using a Slater determinant
- evaluate the energy with the Hamiltonian that includes the electron-electron interactions

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1s}^Z \uparrow(\vec{r}_1) & \phi_{1s}^Z \uparrow(\vec{r}_2) & \dots & \phi_{1s}^Z \uparrow(\vec{r}_N) \\ \phi_{1s}^Z \downarrow(\vec{r}_1) & \phi_{1s}^Z \downarrow(\vec{r}_2) & & \phi_{1s}^Z \downarrow(\vec{r}_N) \\ \vdots & & \ddots & \vdots \\ \phi_N^Z \downarrow(\vec{r}_1) & \phi_N^Z \downarrow(\vec{r}_2) & \dots & \phi_N^Z \downarrow(\vec{r}_N) \end{vmatrix}$$

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

# Lithium

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The antisymmetric 3 electron wavefunction can be written

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \left| \phi_{1s}^{Li} \uparrow, \phi_{1s}^{Li} \downarrow, \phi_{2s}^{Li} \uparrow \right\rangle = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}^{Li} \uparrow(\vec{r}_1) & \phi_{1s}^{Li} \uparrow(\vec{r}_2) & \phi_{1s}^{Li} \uparrow(\vec{r}_3) \\ \phi_{1s}^{Li} \downarrow(\vec{r}_1) & \phi_{1s}^{Li} \downarrow(\vec{r}_2) & \phi_{1s}^{Li} \downarrow(\vec{r}_3) \\ \phi_{2s}^{Li} \uparrow(\vec{r}_1) & \phi_{2s}^{Li} \uparrow(\vec{r}_2) & \phi_{2s}^{Li} \uparrow(\vec{r}_3) \end{vmatrix}$$

There are two possible configurations

$$\left| \phi_{1s}^{Li} \uparrow, \phi_{1s}^{Li} \downarrow, \phi_{2s}^{Li} \uparrow \right\rangle \quad \text{and} \quad \left| \phi_{1s}^{Li} \uparrow, \phi_{1s}^{Li} \downarrow, \phi_{2s}^{Li} \downarrow \right\rangle$$

Construct the Hamiltonian matrix to see which has the lowest energy

# Beryllium

The antisymmetric 4 electron wave function can be written,

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = \left| \phi_{1s}^{Be} \uparrow, \phi_{1s}^{Be} \downarrow, \phi_{2s}^{Be} \uparrow, \phi_{2s}^{Be} \downarrow \right\rangle$$
$$= \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_{1s}^{Be} \uparrow(\vec{r}_1) & \phi_{1s}^{Be} \uparrow(\vec{r}_2) & \phi_{1s}^{Be} \uparrow(\vec{r}_3) & \phi_{1s}^{Be} \uparrow(\vec{r}_4) \\ \phi_{1s}^{Be} \downarrow(\vec{r}_1) & \phi_{1s}^{Be} \downarrow(\vec{r}_2) & \phi_{1s}^{Be} \downarrow(\vec{r}_3) & \phi_{1s}^{Be} \downarrow(\vec{r}_4) \\ \phi_{2s}^{Be} \uparrow(\vec{r}_1) & \phi_{2s}^{Be} \uparrow(\vec{r}_2) & \phi_{2s}^{Be} \uparrow(\vec{r}_3) & \phi_{2s}^{Be} \uparrow(\vec{r}_4) \\ \phi_{2s}^{Be} \downarrow(\vec{r}_1) & \phi_{2s}^{Be} \downarrow(\vec{r}_2) & \phi_{2s}^{Be} \downarrow(\vec{r}_3) & \phi_{2s}^{Be} \downarrow(\vec{r}_4) \end{vmatrix}$$

# Gold

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The antisymmetric 79 electron wave function can be written,

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{79}) = \left| \phi_{1s}^{79} \uparrow (\vec{r}_1), \phi_{1s}^{79} \downarrow (\vec{r}_2), \dots, \phi_{6s}^{79} \uparrow (\vec{r}_{79}) \right\rangle$$

The determinant of an  $N \times N$  matrix has  $N!$  terms.

$$79! = 8.95 \times 10^{116}$$

(more than the atoms in the observable universe)

Start with the valence electrons. Stop adding electrons when the matrix gets too big.

# Pauli exclusion

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The sign of the wave function must change when two electrons are exchanged

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1))$$

If two columns are exchanged, the wave function changes sign.

If two columns are the same, the determinant is zero.

The Pauli exclusion principle only holds in the noninteracting electron approximation when the many electron wave function can be written as a product of single electron wave functions, only one electron can occupy each single electron state.

# Atomic physics summary

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Solutions to the Schrödinger equation accurately describe the observed energy levels in atoms.

We know the equation that needs to be solved but it is intractable.

A common first approximation is the orbital approximation: Assign the electrons to an atomic orbital and a spin antisymmetrized product of spin orbitals.

The energy is then evaluated including the electron-electron interactions.

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Sometimes assumptions have to be made about the core wave functions and the wave functions of the valence electrons are determined numerically.

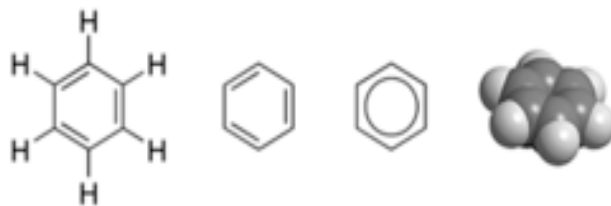
# The full Hamiltonian of a molecule

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

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

This explains life, the universe, and everything!



# Born Oppenheimer approximation

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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)

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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.

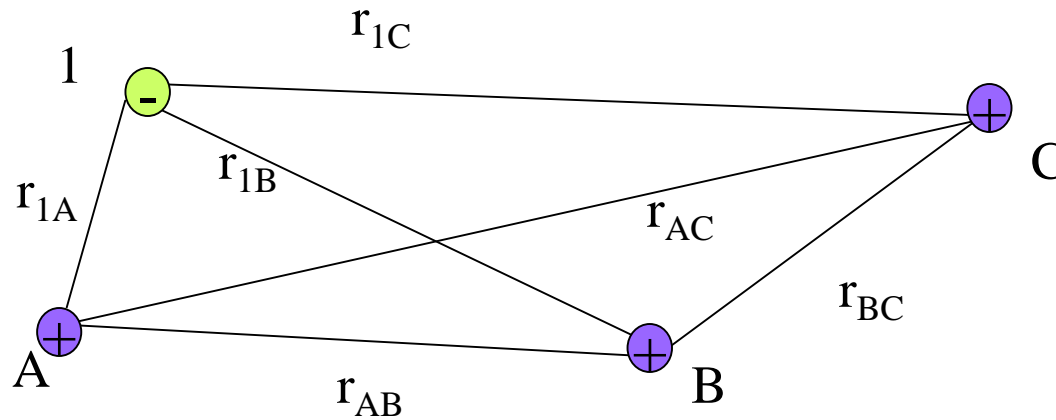
$$H_t(r_1, r_2, \dots, r_n) = H_1(r_1) + H_2(r_2) + \dots + H_n(r_n)$$

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

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

# Molecular orbital Hamiltonian

Fix the positions of the nuclei. Solve the Schrödinger equation for one electron. Find the ground state and the excited states.

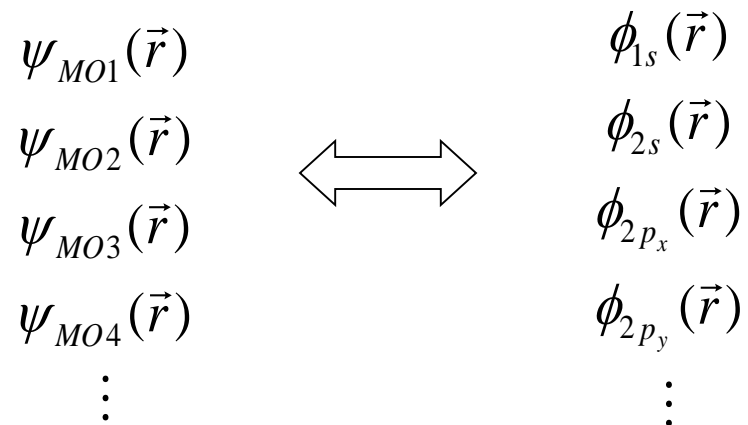


$$H_{MO} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 |r_1 - r_A|}$$

# Molecular orbitals

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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

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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.

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

# Molecular orbitals

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Calculate the energy of a molecular orbital using the electronic Hamiltonian.

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \left| \psi_{MO1} \uparrow, \psi_{MO1} \downarrow, \psi_{MO2} \uparrow, \psi_{MO2} \downarrow, \dots \right\rangle$$

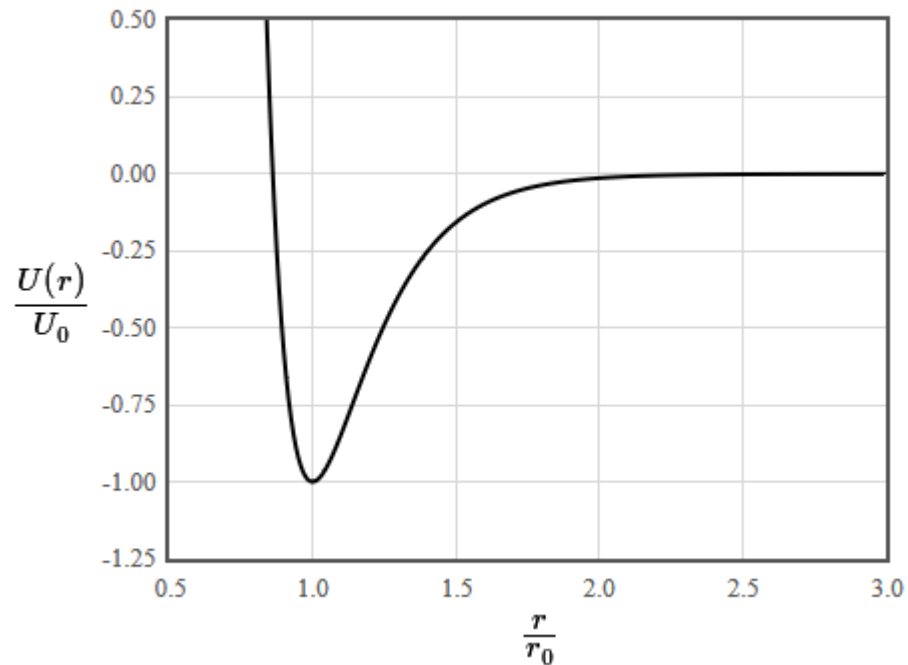
$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

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

# Bond potentials

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



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

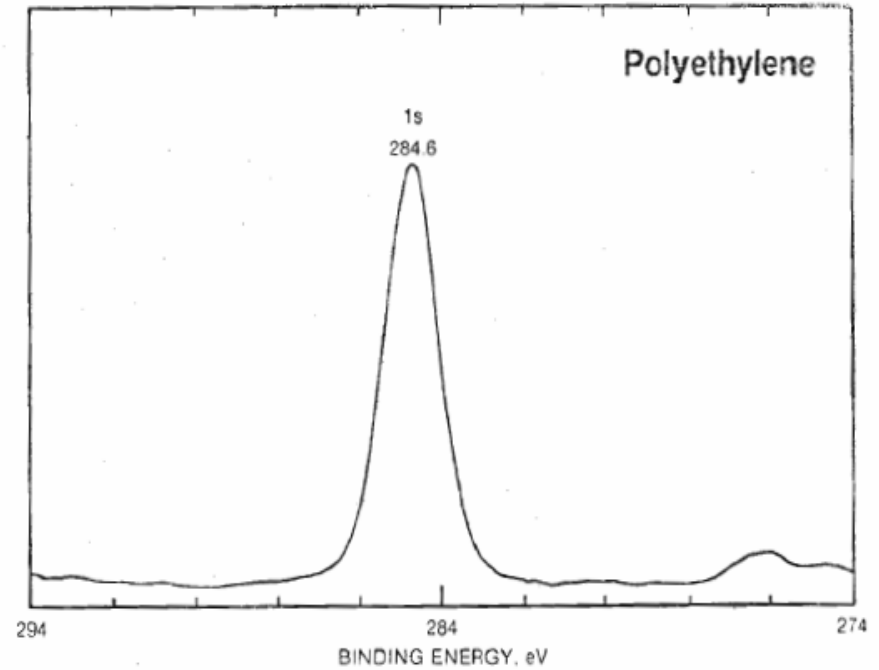
<b>Bondlength (nm) and bond energy (eV)</b>					
Bond	Length	Energy	Bond	Length	Energy
H--H	0.074	4.52	H--C	0.109	4.28
C--C	0.154	3.61	H--N	0.101	4.05
C=C	0.134	6.36	H--F	0.092	5.89
C≡C	0.120	8.70	H--O	0.096	3.79
C--O	0.143	3.73	H--Cl	0.127	4.48
C--S	0.182	2.82	H--Br	0.141	3.79
C--F	0.135	5.06	H--I	0.161	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.
HfC	280	RH1
TiC	284	RH1
WC	288	RH1
C (graphite)	284.6	HJG
(CH <sub>2</sub> ) <sub>n</sub>	285	Φ
Mn(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	285	BCD
SnPh <sub>4</sub>	285	BAL
MeCH <sub>2</sub> NH <sub>2</sub>	285	GHH
Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	285	PFD
MeCH <sub>2</sub> Cl	285	GHH
MeCH <sub>2</sub> OH	285	GHH
MeCH <sub>2</sub> OEt	285	GHH
MeCH <sub>2</sub> OOCMe	285	GHH
CS <sub>2</sub>	285	GHH
Fe(CO) <sub>5</sub>	285	BC1
Me <sub>2</sub> CO	285	GHH
(NH <sub>2</sub> ) <sub>2</sub> CO	285	GHH
C <sub>5</sub> F <sub>6</sub>	285	GHH
MeCOONa	285	GHH
MeCOOEt	285	GHH
MeCOOH	285	GHH
Na <sub>2</sub> CO <sub>3</sub>	285	GHH
NaHCO <sub>3</sub>	285	GHH
CO	285	BC1
CO <sub>2</sub>	285	GHH
(CHFCH <sub>2</sub> ) <sub>n</sub>	285	CFK
(CHFCHF) <sub>n</sub>	285	CFK
(CHFCHF <sub>2</sub> ) <sub>n</sub>	285	CFK
(CF <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub>	285	CFK
(CF <sub>2</sub> CHF) <sub>n</sub>	285	CFK
(CF <sub>2</sub> ) <sub>n</sub>	285	CFK
CF <sub>3</sub> COONa	285	GHH
CCl <sub>4</sub>	285	GHH
CF <sub>3</sub> COMe	285	GHH
CF <sub>3</sub> COOEt	285	GHH

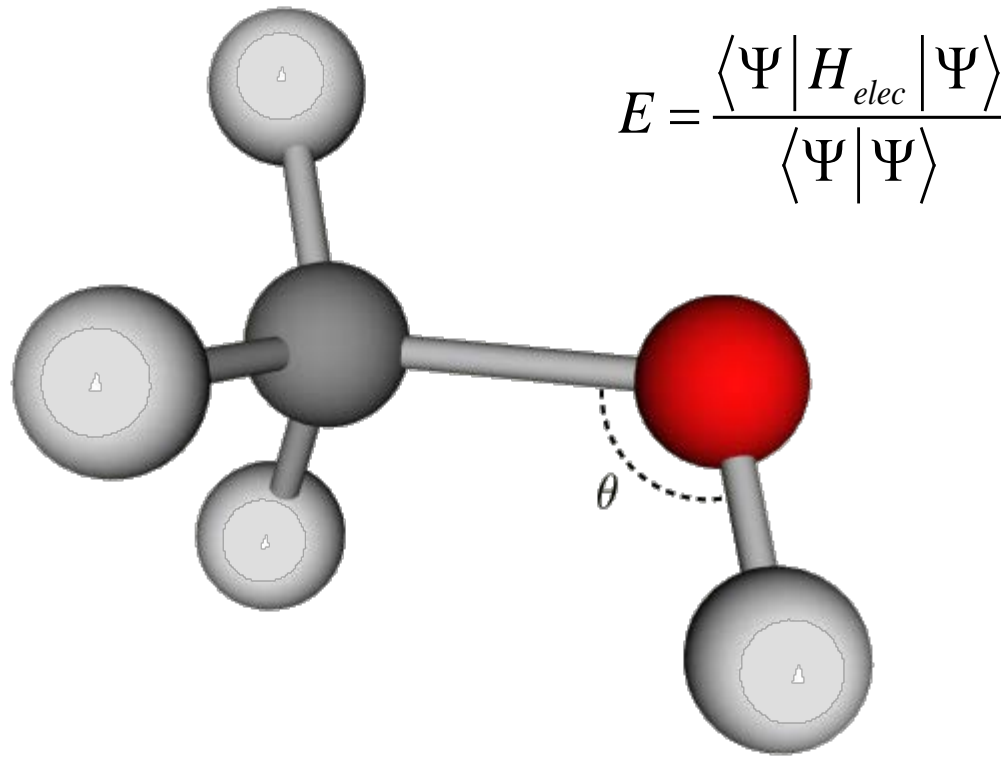




# Bond angles

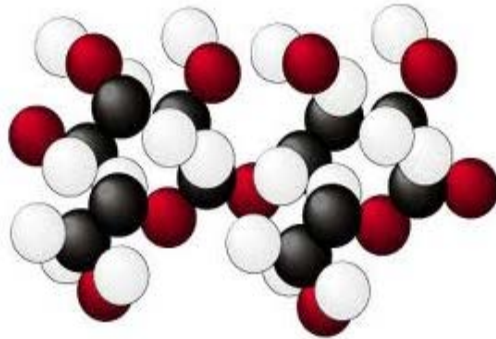
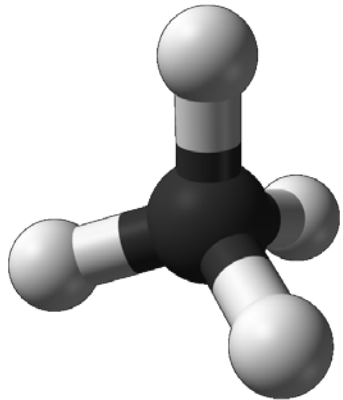
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Find the angle that minimizes the energy.

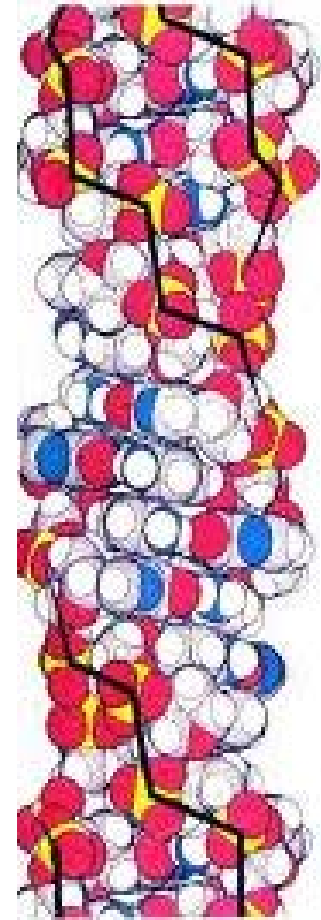
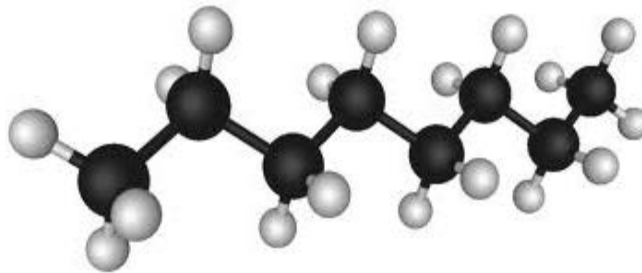
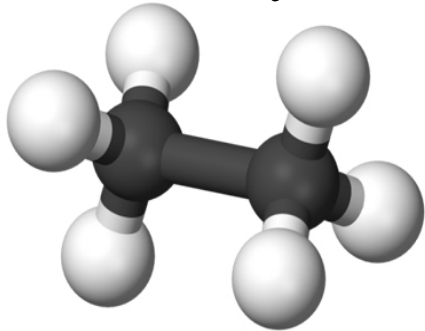


# Shape of a molecule

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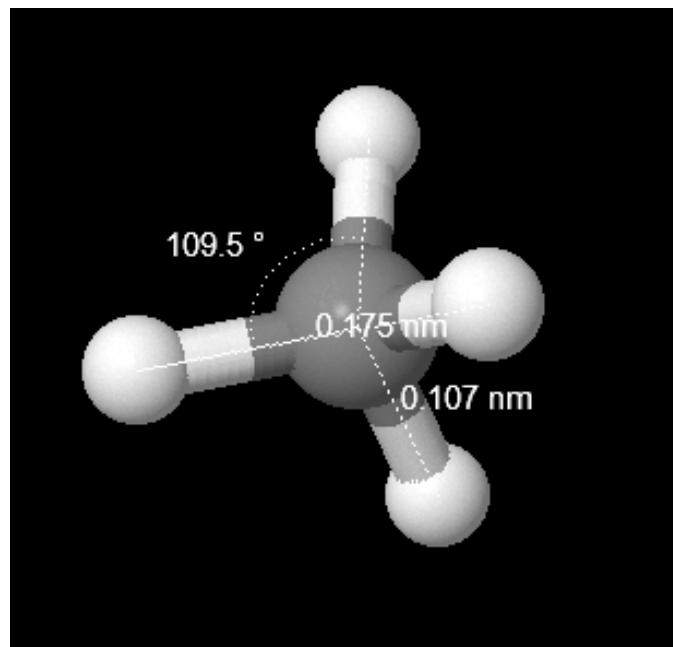


$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$



# Shape of a molecule

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

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

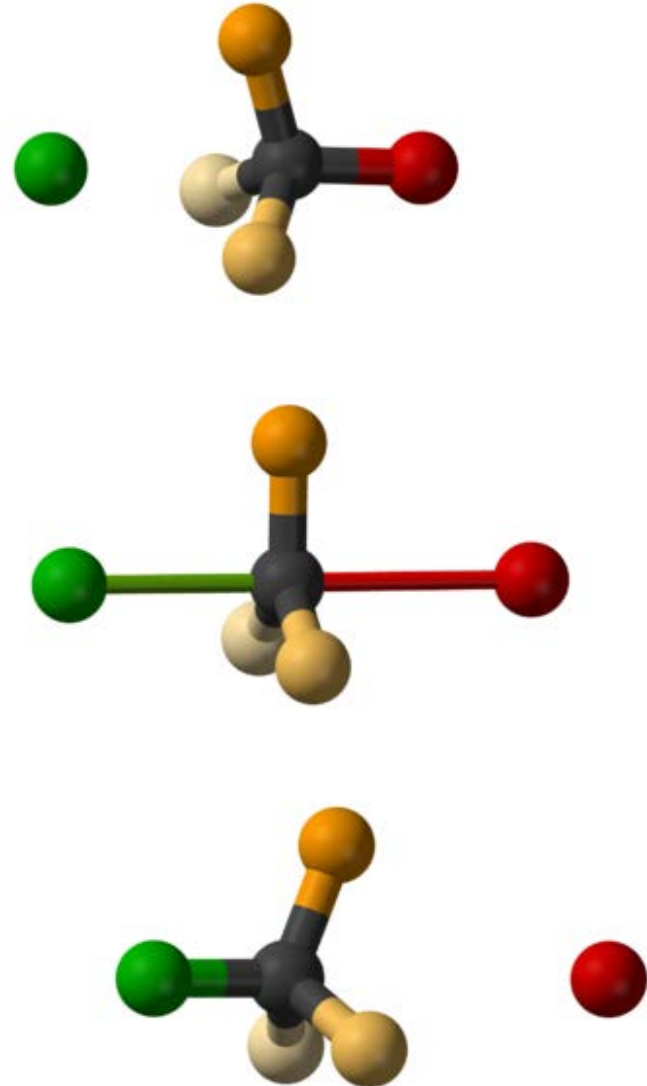
# Chemical reactions

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Calculate the energy at every stage of the reaction.

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

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





# The molecular orbital can be found by: Linear Combination of Atomic Orbitals

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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  $\phi_n$  are atomic orbitals.

# Molecular orbitals of H<sub>2</sub>

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The molecular orbital Hamiltonian for H<sub>2</sub> 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 H<sub>2</sub>

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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 H<sub>2</sub>

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

Roothaan equations: 
$$\begin{bmatrix} H_{AA} & H_{AB} \\ H_{AB}^* & H_{BB} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{AA} & S_{AB} \\ S_{AB}^* & S_{BB} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

Hamiltonian matrix

Overlap matrix

$$S \approx \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$H_{AA} = H_{BB}$$

# Molecular orbitals of H<sub>2</sub>

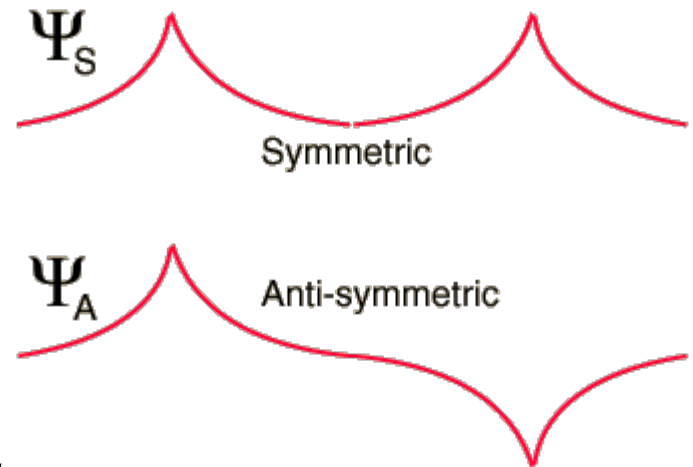
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$$\begin{bmatrix} H_{AA} & H_{AB} \\ H_{AB}^* & H_{AA} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

The eigenvalues and eigenfunctions are:

$$E_{\pm} = H_{AA} \pm H_{AB}$$

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



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

# Molecular orbitals of H<sub>2</sub>

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

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

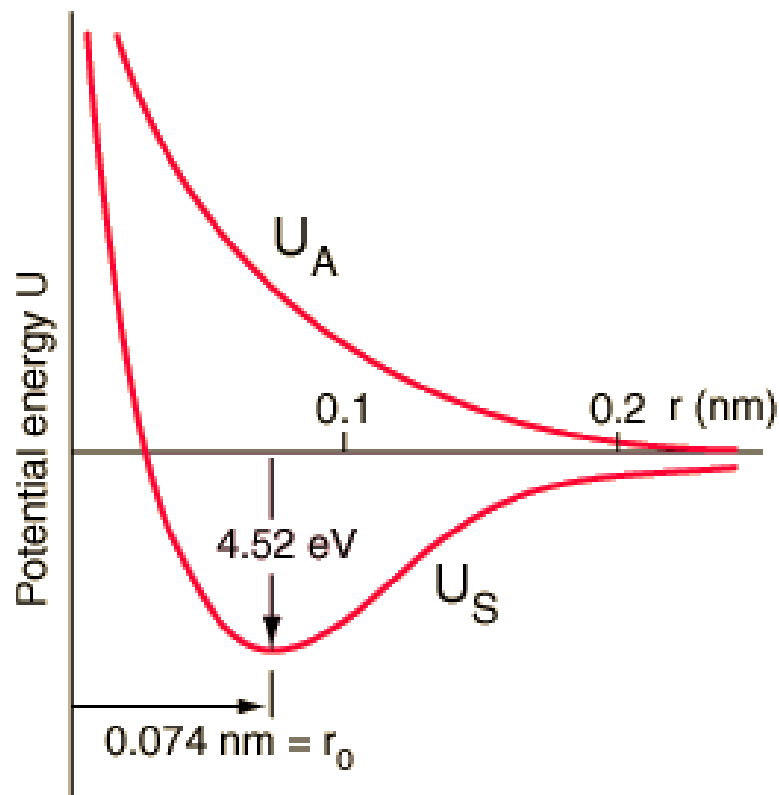
$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{2\sqrt{2}} \left( \phi_{1sA}^H(\vec{r}_1) \phi_{1sA}^H(\vec{r}_2) + \phi_{1sA}^H(\vec{r}_1) \phi_{1sB}^H(\vec{r}_2) + \phi_{1sA}^H(\vec{r}_2) \phi_{1sB}^H(\vec{r}_1) + \phi_{1sB}^H(\vec{r}_1) \phi_{1sB}^H(\vec{r}_2) \right) (\uparrow\downarrow - \downarrow\uparrow)$$

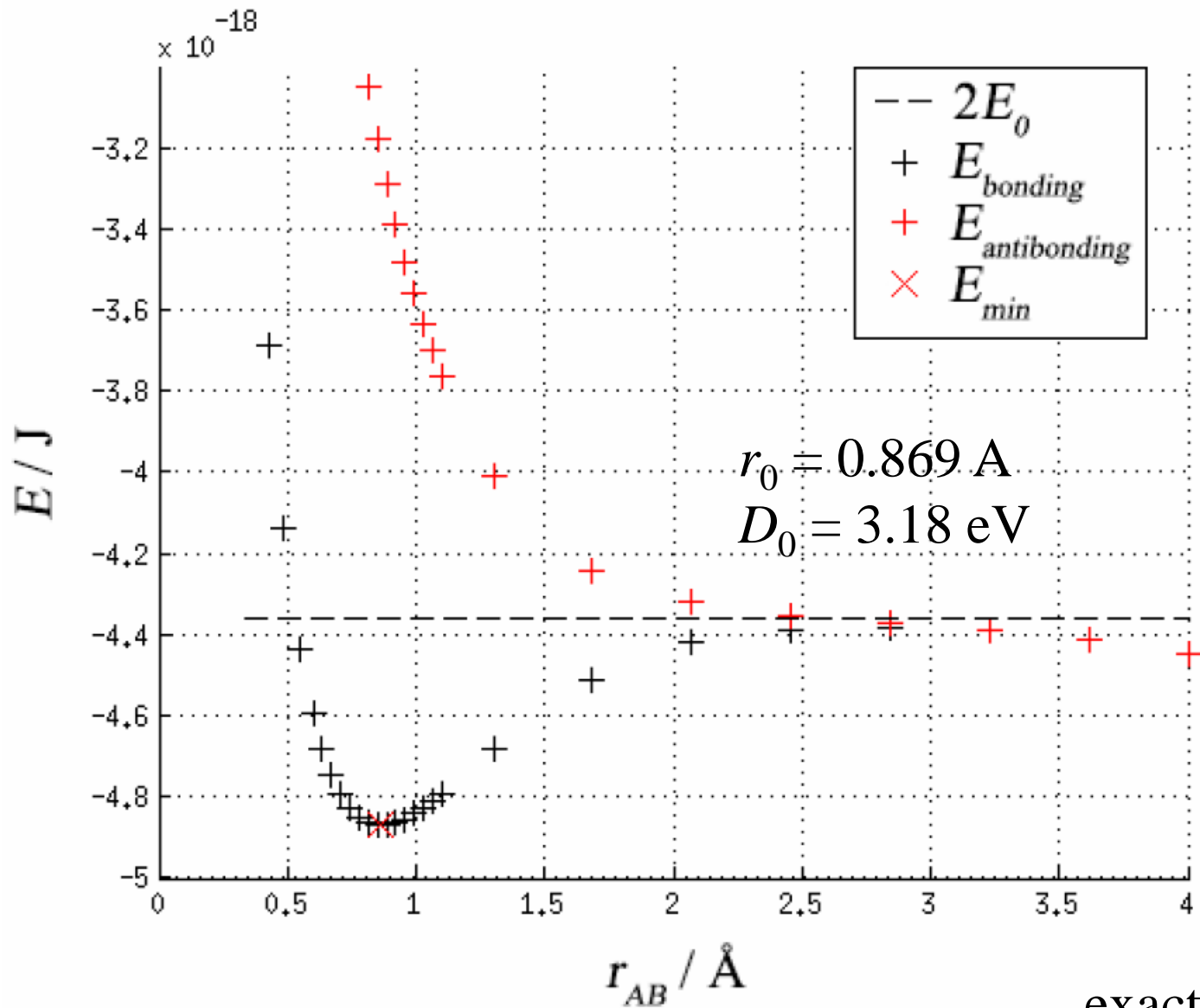
Use this wave function including the electron-electron interaction to calculate the bond potential.

# Student project: Draw the Bond potential of H<sub>2</sub>

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

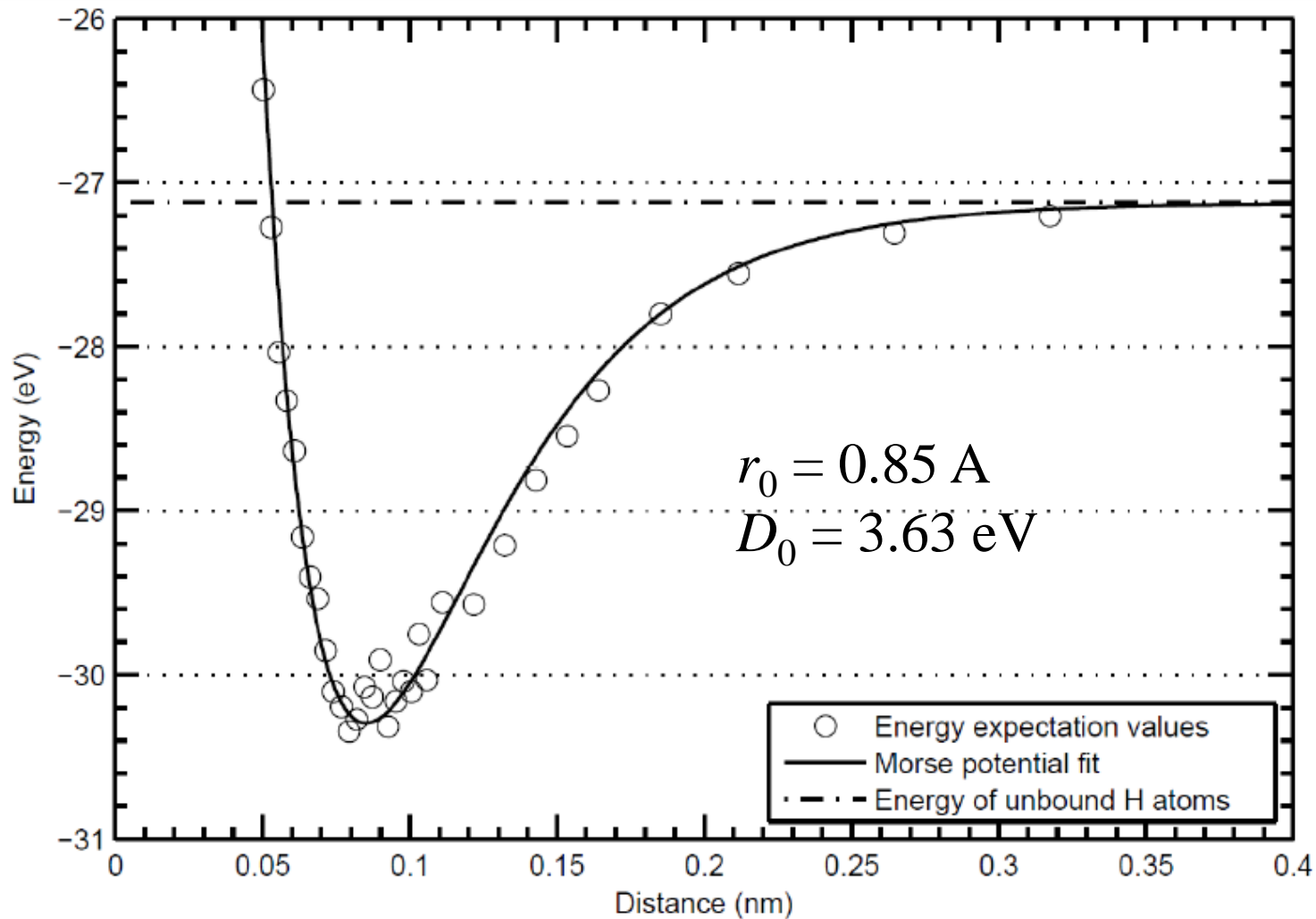




exact values

$r_0 = 0.74 \text{ \AA}$

$D_0 = 4.52 \text{ eV}$



# Homonuclear diatomic molecules

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

All homonuclear diatomic molecules use the molecular orbitals of  $\text{H}_2$ .

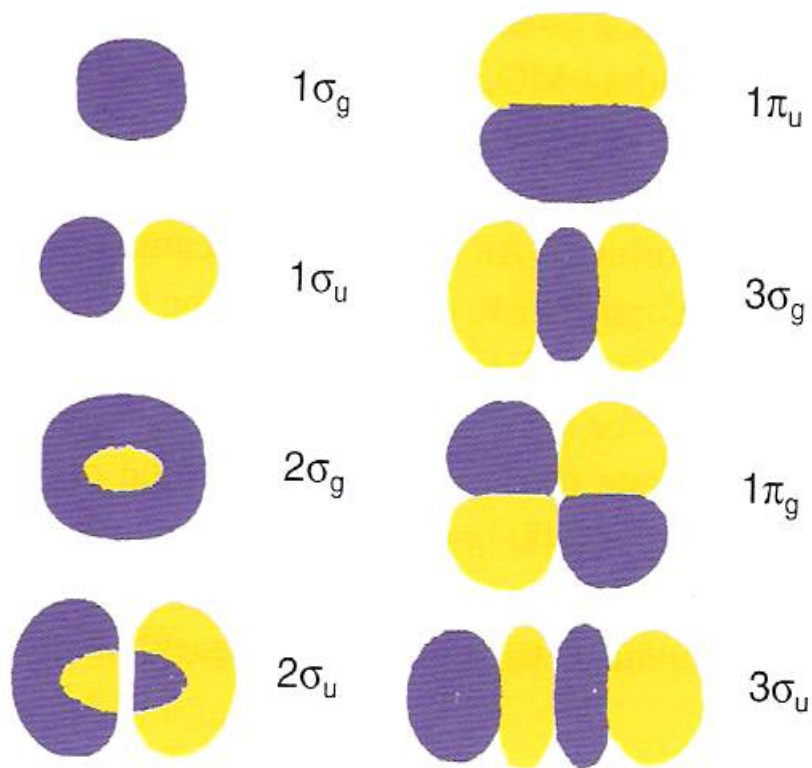
$$\psi_{mo} = c_1 \phi_{1s,A}^Z + c_2 \phi_{1s,B}^Z + c_3 \phi_{2s,A}^Z + c_4 \phi_{2s,B}^Z + c_5 \phi_{2p_x,A}^Z + c_6 \phi_{2p_x,B}^Z + \dots$$

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 <sup>a</sup>	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 <sup>d</sup>	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 <sup>d</sup>	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