

# Hydrogen Molecule

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# Hydrogen molecule

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

$$H_{elec\_red} = \sum_{i=1,2} \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \right]$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\psi(\vec{r}_2)$$

# Molecular orbitals of $\text{H}_2^+$

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The Hamiltonian for  $\text{H}_2^+$  is,

$$H_{\text{mo}}^{\text{H}_2} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_B|}$$

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

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

What about spin?

# Molecular orbitals of $\text{H}_2^+$

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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 $\text{H}_2^+$

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

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 $\text{H}_2^+$

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

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

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

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

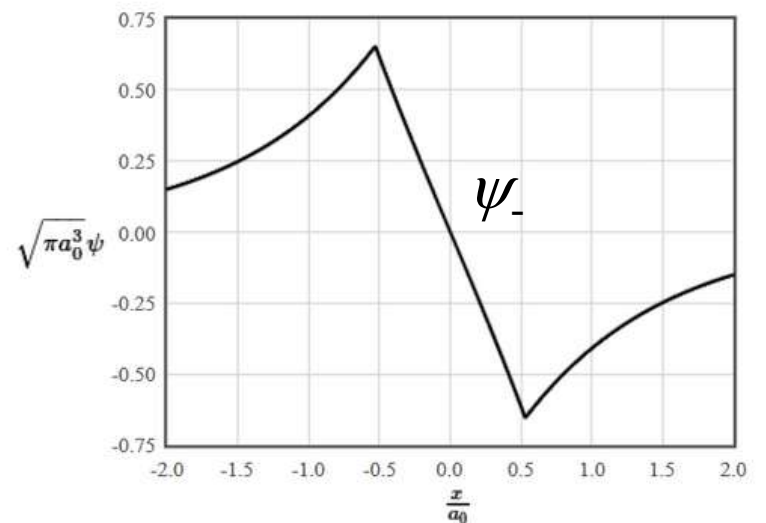
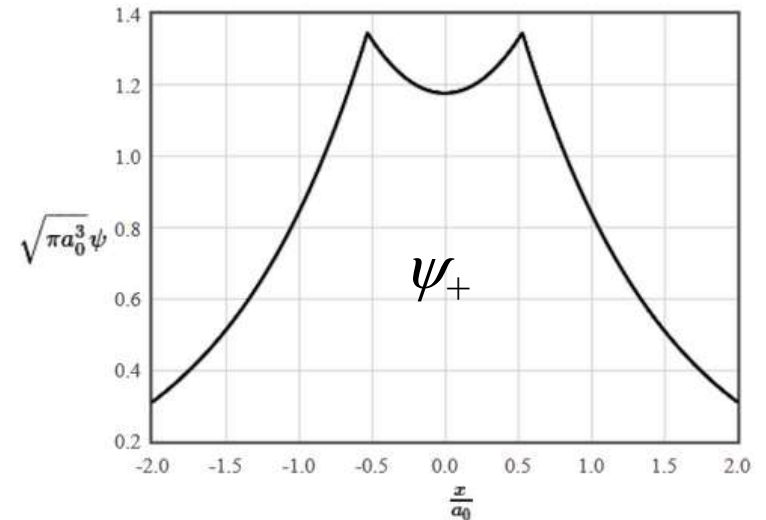
# Molecular orbitals of $\text{H}_2^+$

The eigen values and eigen functions are

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

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

Both  $H_{11}$  and  $H_{12}$  are negative  $E_+ < E_-$



## Molecular orbitals of the molecular ion $\text{H}_2^+$

The molecular ion  $\text{H}_2^+$  consists of one electron and two protons. The molecular orbital Hamiltonian in this case is,

$$H_{\text{mo}}^{\text{H}_2^+} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_B|}, \quad (1)$$

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,

$$H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}. \quad (2)$$

[http://lampx.tugraz.at/~hadley/ss1/molecules/hueckel/mo\\_h2\\_plus.php](http://lampx.tugraz.at/~hadley/ss1/molecules/hueckel/mo_h2_plus.php)



# Determining the matrix elements $S_{11}$ , and $S_{12}$

$$S_{12} = \langle \phi_{1s}(\vec{r} - \vec{r}_1) | \phi_{1s}(\vec{r} - \vec{r}_2) \rangle$$

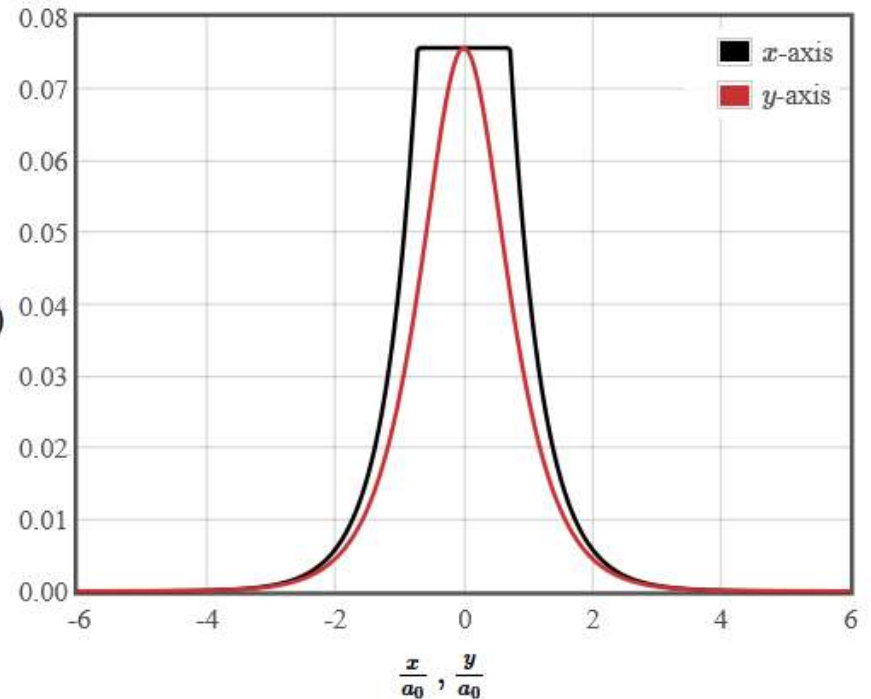
$$a_0^3 \phi_{1s}(\vec{r} - \vec{r}_1) \phi_{1s}(\vec{r} - \vec{r}_2)$$

```
<script>
var a0 = 5.2917721E-11; // Bohr radius in meters
var pi = Math.PI;
var Zeff = 1; // effective nuclear charge
var x1 = -0.38E-10; // position of nucleus 1
var x2 = 0.38E-10; // position of nucleus 2

function ao_1s(x,y,z,xi,yi,zi,Za) { //the 1s atomic orbital
  r = Math.sqrt(Math.pow(x-xi,2)+Math.pow(y-yi,2)+Math.pow(z-zi,2));
  return
  Math.sqrt(Math.pow(Za,3)/(pi*Math.pow(a0,3)))*Math.exp(-Za*r/a0);
}

S12 = 0;
N = 1000000; //number of random points

for (i=0; i<N; i++) {
  x = 8*a0*(0.5-Math.random());
```



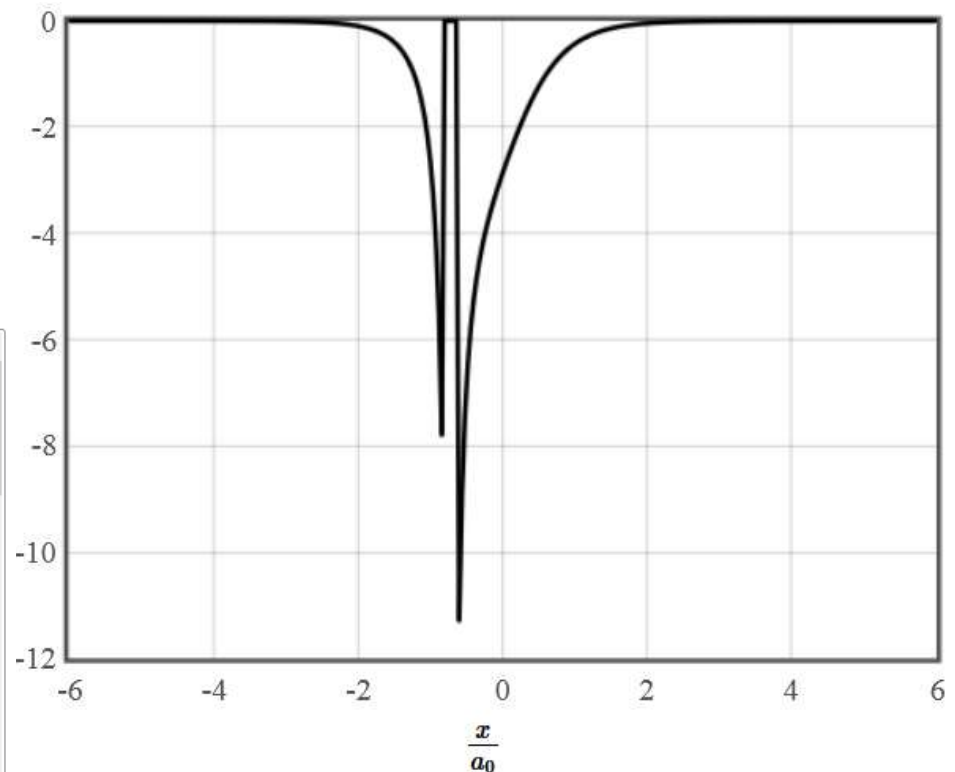
# Determining the matrix elements $H_{11}$ , $H_{12}$

$$H_{12} = \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_2) \right\rangle$$

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<script>
var a0 = 5.2917721E-11; // Bohr radius in meters
var pi = Math.PI;
var ec = 1.60217733E-19; //electron charge
var eps0 = 8.854187817E-12; //permittivity constant
var delta = a0/10;
var Zeff = 1; // effective nuclear charge
var E1 = -Zeff*Zeff*2.17987e-18; // E1 in Joules
var x1 = -0.38E-10; // position of nucleus 1
var x2 = 0.38E-10; // position of nucleus 2

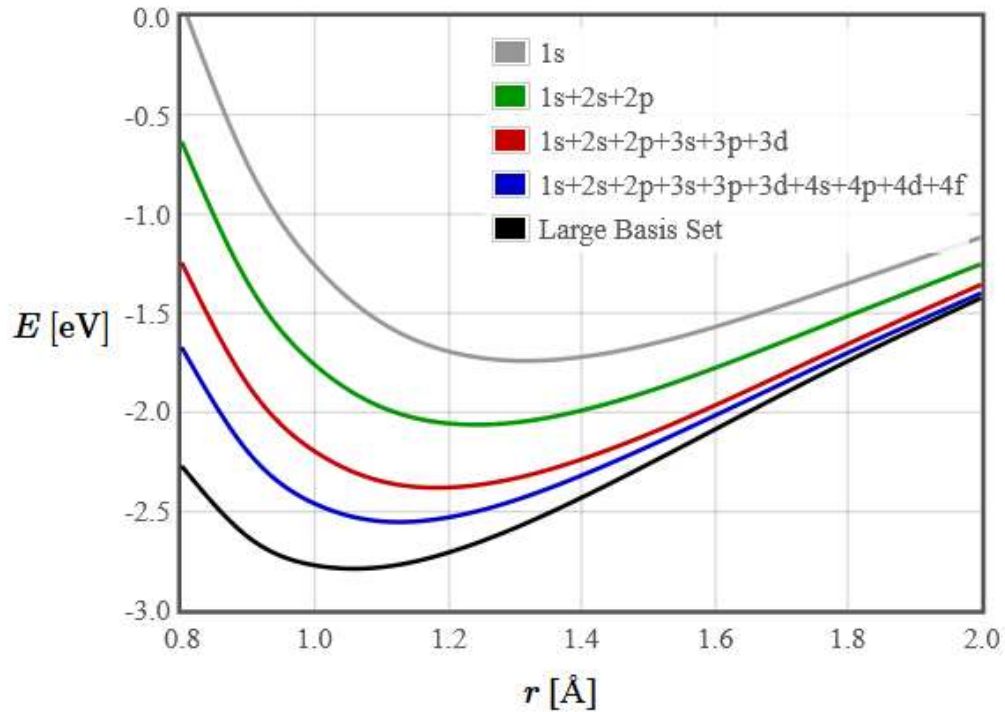
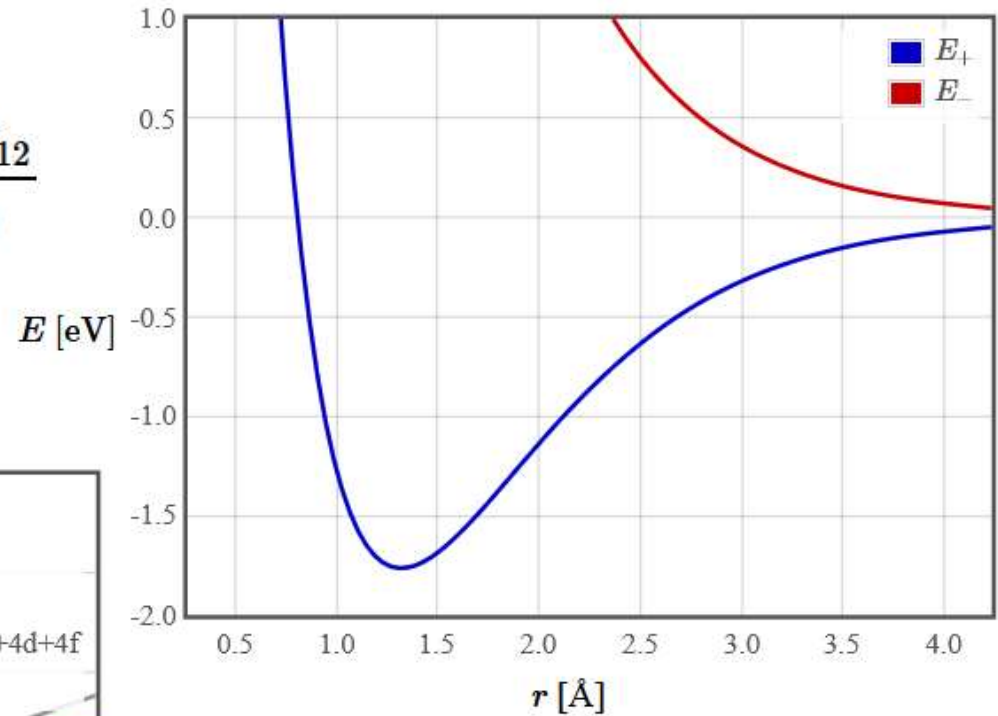
function H(x,y,z,x1,y1,z1,delta) { //Heaviside step function
function
  r = Math.sqrt(Math.pow(x-x1,2)+Math.pow(y-y1,2)+Math.pow(z-z1,2));
  d = r - delta;
  if (d<0) {hv = 0;}
  if (d==0) {hv = 0.5;}
  if (d>0) {hv = 1;}
  return hv;

```



# H<sub>2</sub><sup>+</sup> bond potential

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



# 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).

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

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

$$H_{\text{elec}}^{H_2} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_B|} \\ - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_2 - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r}_2 - \vec{r}_B|} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_A - \vec{r}_B|}.$$

$$E = \frac{\langle \Psi | H_{\text{elec}}^{H_2} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

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

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