

Many electron atoms

Many electrons

Consider a gold atom (79 electrons)

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx_1^2} + \dots + \frac{d^2}{dz_{79}^2} \right) \Psi - \frac{79e^2}{4\pi\epsilon_0 r_j} \Psi + \frac{e^2}{4\pi\epsilon_0 r_{ij}} \Psi$$

$\nearrow \qquad \nearrow \qquad \nearrow$

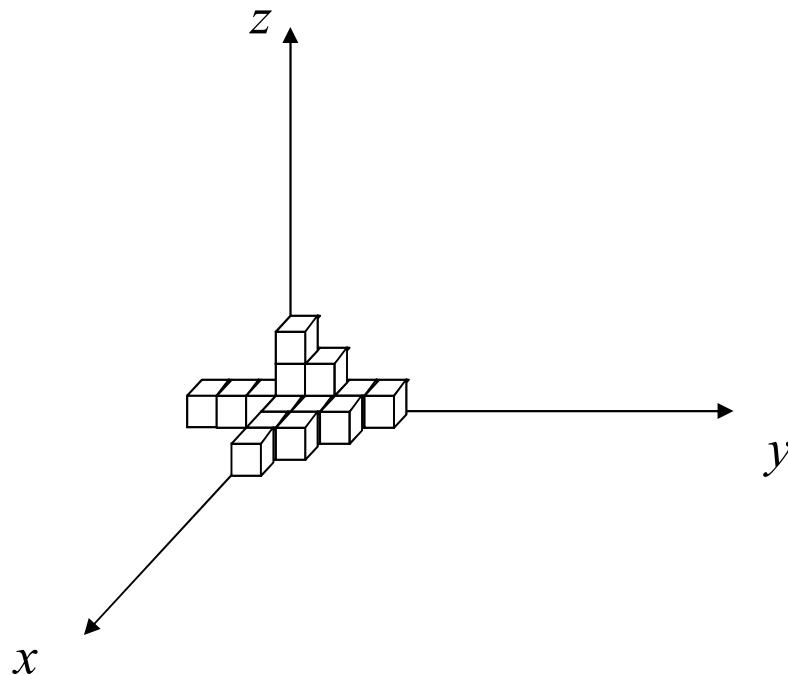
$3 \times 79 = 237 \text{ terms} \qquad 79 \text{ terms} \qquad \frac{79 \times 78}{2} = 3081 \text{ terms}$

$\Psi(x_1, y_1, z_1, \dots, x_{79}, y_{79}, z_{79}, t)$ is a complex function in 237 dimensions

$|\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2$ is the joint probability density of finding an electron at position r_1, r_2, \dots, r_N .

Numerical solution of the Schrödinger equation for one electron

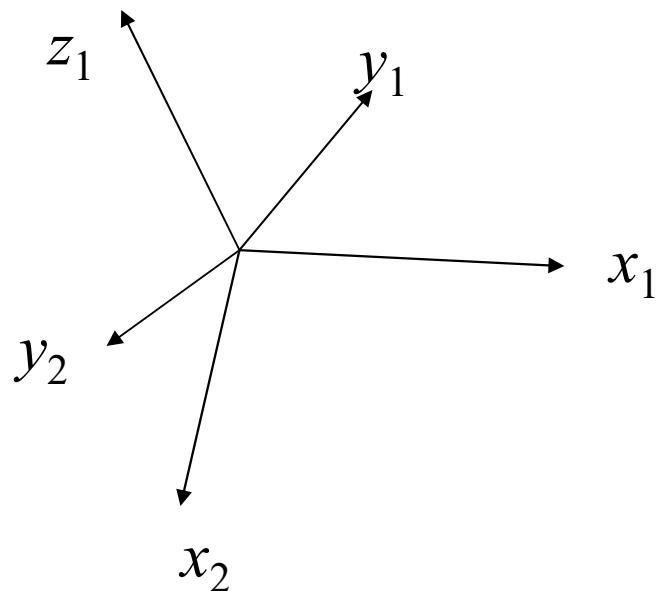
$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi - \frac{e^2}{4\pi\epsilon_0 r} \Psi$$



Discretize Ψ to solve numerically. For one electron $\sim 10^6$ elements are needed.

Numerical solution for many electrons

For a numerical solution, divide Hilbert space along each axis into 100 divisions.



$$100^{237} = 10^{474}$$

There are 10^{68} atoms in the
Milky Way galaxy

There are $\sim 10^{80}$ atoms in the
observable universe

Intractable problem

We know the equation that has to be solved. We know how to solve it but we don't have the computer resources to calculate the answer.

A Matlab that will calculate the time evolution of an n -electron atom

```
clear all
cic % Programm zur numerischen Berechnung der zeitabhängigen Wellenfunktion eines Atoms mit Z Elektronen
      % Programm funktioniert mit beliebiger Anzahl an Elektronen

Z = 1; % Ordnungs-/Elektronen-/Protonenzahl des Atomes
e0 = 8.85418781762*10^(0-12); % Permittivität
me = 9.10938291*10^(0-31); % Elektronenmasse
h = 6.62606957*10^(0-34); % planckes Wirkungsquantum
e = 1.602176565*10^(0-19); % Elementarladung
a0 = 0.52917721092*10^(0-10); % bohrscher Radius
I = [-1:0.02:1].*(a0.*4); % Intervall zur numerischen Auswertung Differential
IO = I(2:(end-1));
I_1= I(1:(end-2));
I1 = I(3:end);
Ik = [I_1;I1;I_1];
t = [0:0.01:1]; % Intervall Zeit
dIndizes = 2:(numel(I)-1); % Vektor zur Indizierung für nicht betroffene x,y,z 1.Ableitung
ddIndizes = 1:(numel(I)-2); % Vektor zur Indizierung für nicht betroffene x,y,z 2.Ableitung

for k=1:(3.*Z)
    dimension = ones(1,3.*Z); % für reshape, richtet das Intervall in die gewünschte Richtung (Dimension) aus
    dimension(k) = numel(IO);
    matrix = ones(1,3.*Z).*numel(IO); % für repmat, macht aus dem Vektor eine Matrix in 3Z Dimensionen
    matrix(k) = 1;
    X0 = repmat(reshape(IO,dimension),matrix); % 3Z dimensionale Matrix für jede Richtung; enthält Intervall für phi("x")
    matrizen(k) = X0; % abspeichern der Intervallmatrizen in eine Zelle, zum leichteren auslesen
end

for k=1:(3.*Z)
    matrizen=matrizen{:};
    for m=1:3
        dimension = ones(1,3.*Z); % für reshape, richtet das Intervall in die gewünschte Richtung (Dimension) aus
        dimension(k) = numel(1:IO);
        matrix = ones(1,3.*Z).*numel(1:IO); % für repmat, macht aus dem Vektor eine Matrix in 3Z Dimensionen
        matrix(k) = 1;
        X0 = repmat(reshape(Ik(m,:),dimension),matrix); % 3Z dimensionale Matrix für jede Richtung; enthält Intervall für phi("x+dx/x-x-dx")
        matrizen(k)=X0;
        phi = exp(0-sqrt(matrizen(1).^2+matrizen(2).^2+a0)); % Bsp. für H; allgemein : xk=3*(k-1)+1, yk=3*(k-1)+2, zk=3*k
        if m==2 % Bestimmung des Vorfaktors
            a=-2;
        else
            a=1;
        end
        if k==1 & m==2 % Abspeicherung von phi0
            phi0=phi;
        end
        if k==1 & m==1
            ddphi_sum=zeros(size(phi));
        end
        ddphi_sum=ddphi_sum+(a.*phi)./(0.02.*4.*a0).^2; % Summenbildung über d2phi/dx2 = (phi(x+dx)-2*phi(x)+phi(x-dx))/(Schrittweite des Intervalle)
    end
end

for k=1:2 % Berechnung der Abstände Elektron-Kern + Summenbildung aller Terme
    rNE = (matrizen0(((k-1).*3+1)).^2+matrizen0(((k-1).*3+2)).^2+matrizen0(((k).*3)).^2).^(1./2);
    if k==1
        rNE_sum = zeros(size(rNE));
    end
    rNE_sum = rNE_sum + 1./rNE;
    if Z==1 % Für Z=1 existiert keine Elektron-Elektron- Wechselwirkung --> 0
        rEE_sum = zeros(size(rNE_sum));
    end
end

for k=1:(2-1) % Berechnung der Abstände Elektron-Elektron + Summenbildung aller Terme
    for m=2:2
        rEE = ((matrizen0(((k-1).*3+1))-matrizen0((m-1).*3+1))).^2+((matrizen0(((k-1).*3+2))-matrizen0((m-1).*3+2))).^2+((matrizen0(((k).*3))-matrizen0((m).*3)));
        if k==1 & m==2
            rEE_sum = zeros(size(rEE));
        end
        rEE_sum = rEE_sum + 1./rEE;
    end
end

phi_dt = (rEE_sum.*((e.^2./(h.*2.*e0)).*phi0)./(1i) - (rNE_sum.*((Z.*e.^2./(h.*2.*e0)).*phi0)./(1i) - ((h./(4.*pi.*me)).*ddphi_sum)./(1i)); % Wellenfunktion d(r
for k=1:numel(t)
    PHI_t(k) = phi_dt.*t(k); % Lösung der zeitabhängigen Wellenfunktion; die Wellenfunktion zum Zeitpunkt t(k) ist in PHI_t(k) gespeichert
end
```

http://lamp.tu-graz.ac.at/~hadley/ss1/studentpresentations/2011/n_electrons.m

Quantum computation

Sometimes it is possible to map one intractable problem onto another.

If you map an intractable problem onto a system of interacting electrons and then measure the energy levels of the electron system, you can find solutions to the intractable problem.

Many-electron systems

In such a quantum system, the repeated interactions between particles create quantum correlations, or entanglement. As a consequence, the wave function of the system is a complicated object holding a large amount of information, which usually makes analytical calculations impractical. In fact, many-body theoretical physics ranks among the most computationally intensive fields of science.

http://en.wikipedia.org/wiki/Many-body_problem

The Central Dilemma of Solid State Physics

From a fundamental point of view it is impossible to describe electrons in a metal correctly - Ashcroft and Mermin

The Schrödinger explains everything but can explain nothing.

Many electrons

$$-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx_1^2} + \dots + \frac{d^2}{dz_{79}^2} \right) \Psi - \sum_j \frac{79e^2}{4\pi\epsilon_0 r_j} \Psi + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \Psi = E\Psi$$

The solutions to the reduced Hamiltonian are products of atomic orbitals.

Include electron - electron interactions with Slater's rules.

Orbital approximation

- Assign the electrons to an atomic orbital and a spin, use Slater's rules
- Construct an antisymmetrized wave function using a Slater determinant
- Evaluate the energy with the Hamiltonian that includes the electron-electron interactions

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

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

Electron configurations

13	Al	aluminium	$1s^2 2s^2 2p^6 3s^2 3p^1$	$= [Ne] 3s^2 3p^1$
14	Si	silicon	$1s^2 2s^2 2p^6 3s^2 3p^2$	$= [Ne] 3s^2 3p^2$
15	P	phosphorus	$1s^2 2s^2 2p^6 3s^2 3p^3$	$= [Ne] 3s^2 3p^3$
16	S	sulfur	$1s^2 2s^2 2p^6 3s^2 3p^4$	$= [Ne] 3s^2 3p^4$
17	Cl	chlorine	$1s^2 2s^2 2p^6 3s^2 3p^5$	$= [Ne] 3s^2 3p^5$
18	Ar	argon	$1s^2 2s^2 2p^6 3s^2 3p^6$	$= [Ne] 3s^2 3p^6$
19	K	potassium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$= [Ar] 4s^1$
20	Ca	calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$= [Ar] 4s^2$
21	Sc	scandium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	$= [Ar] 3d^1 4s^2$
22	Ti	titanium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	$= [Ar] 3d^2 4s^2$
23	V	vanadium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	$= [Ar] 3d^3 4s^2$
24	Cr	chromium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	$= [Ar] 3d^5 4s^1$
25	Mn	manganese	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	$= [Ar] 3d^5 4s^2$
26	Fe	iron	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	$= [Ar] 3d^6 4s^2$
27	Co	cobalt	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	$= [Ar] 3d^7 4s^2$
28	Ni	nickel	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$	$= [Ar] 3d^8 4s^2$
29	Cu	copper	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	$= [Ar] 3d^{10} 4s^1$
30	Zn	zinc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	$= [Ar] 3d^{10} 4s^2$

Filling of electron shells



Why isn't Ni $3d^9 4s^1$ or $3d^{10}$?

You can evaluate the energy of any electron configuration.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{28}) = \left| \phi_{1s}^{Z_{eff}} \uparrow (\vec{r}_1), \phi_{1s}^{Z_{eff}} \downarrow (\vec{r}_2), \dots, \phi_{3d}^{Z_{eff}} \uparrow (\vec{r}_{27}), \phi_{4s}^{Z_{eff}} \uparrow (\vec{r}_{28}) \right\rangle$$

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

Hund's rules

Pauli exclusion

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

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

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

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 and construct an antisymmetrized product of spin orbitals using a Slater determinant.

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

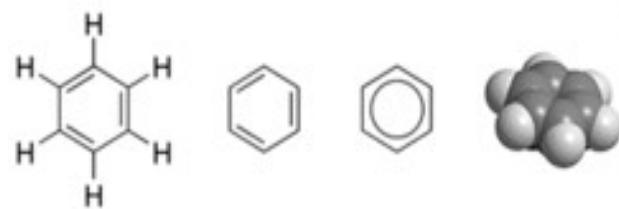
$$E = \frac{\langle \Psi | H_{total} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Molecules

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.

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

Separation of variables (Trennung der Veränderlichen)

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

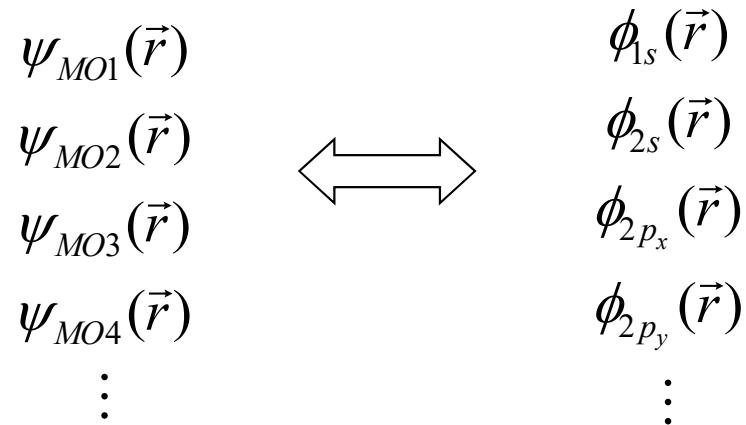
$$H_{elec_red} = \sum_i \left(\frac{-\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \right) = \sum_i H_{MO}$$

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.

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

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.

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

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,

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

Here ϕ_n are atomic orbitals with Z_{eff} .

Hydrogen Molecule

Hydrogen molecule

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

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

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

Molecular orbitals of 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.

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

What about spin?

Molecular orbitals of H_2^+

The time independent Schrödinger equation,

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

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

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

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

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

Two equations with two unknowns: c_1 and c_2

Molecular orbitals of H_2^+

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

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⁺

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

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

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

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

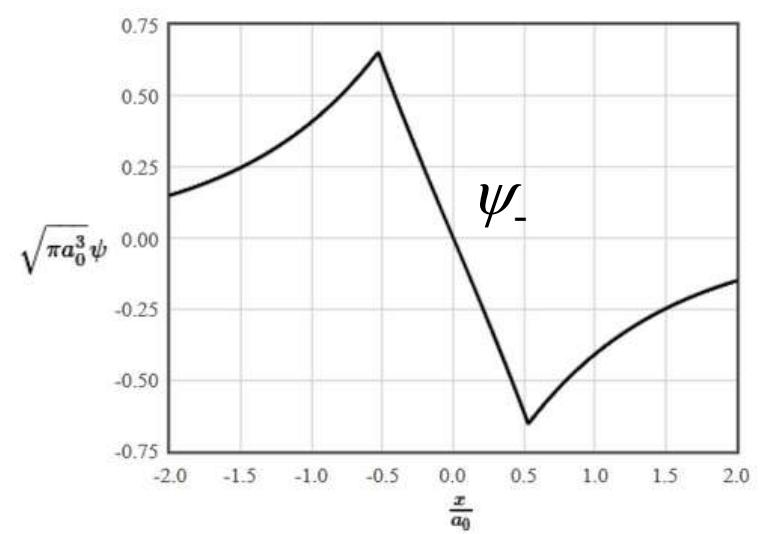
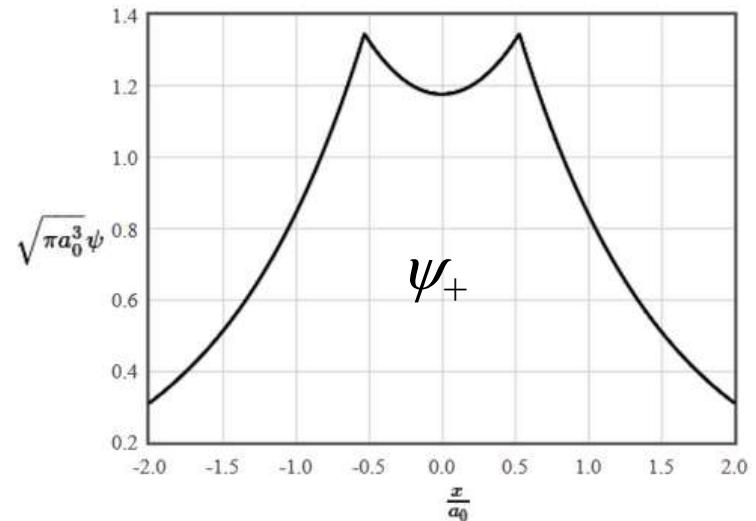
Molecular orbitals of H_2^+

The eigen values and eigen functions are

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

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

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



Molecular orbitals of the molecular ion H₂⁺

The molecular ion H₂⁺ consists of one electron and two protons. The molecular orbital Hamiltonian in this case is,

$$H_{\text{mo}}^{H_2^+} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_B|}, \quad (1)$$

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

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

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

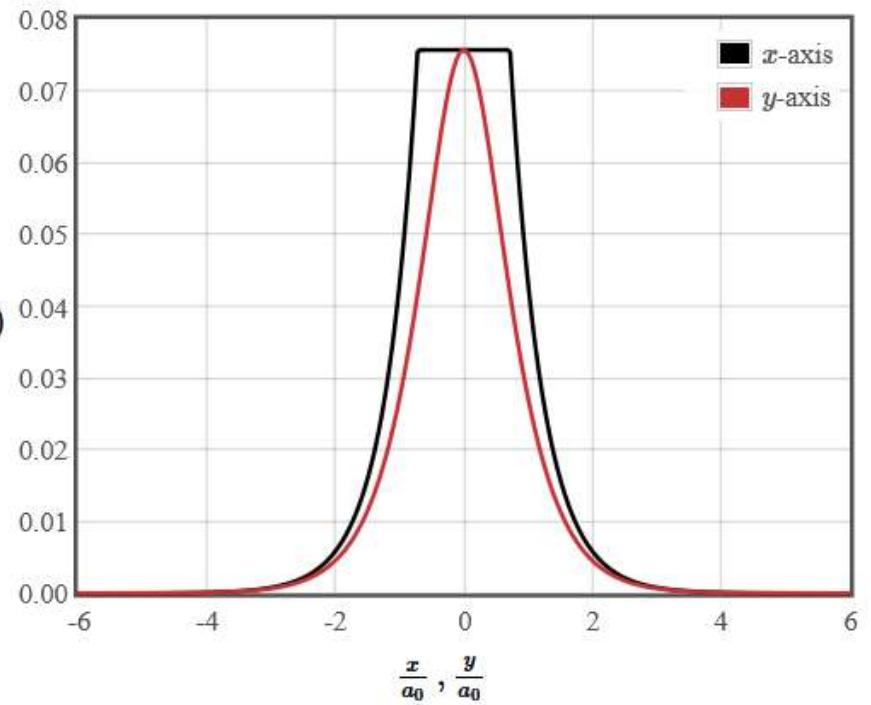
$$a_0^3 \phi_{1s}(\vec{r} - \vec{r}_1) \phi_{1s}(\vec{r} - \vec{r}_2)$$

```
<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);
}

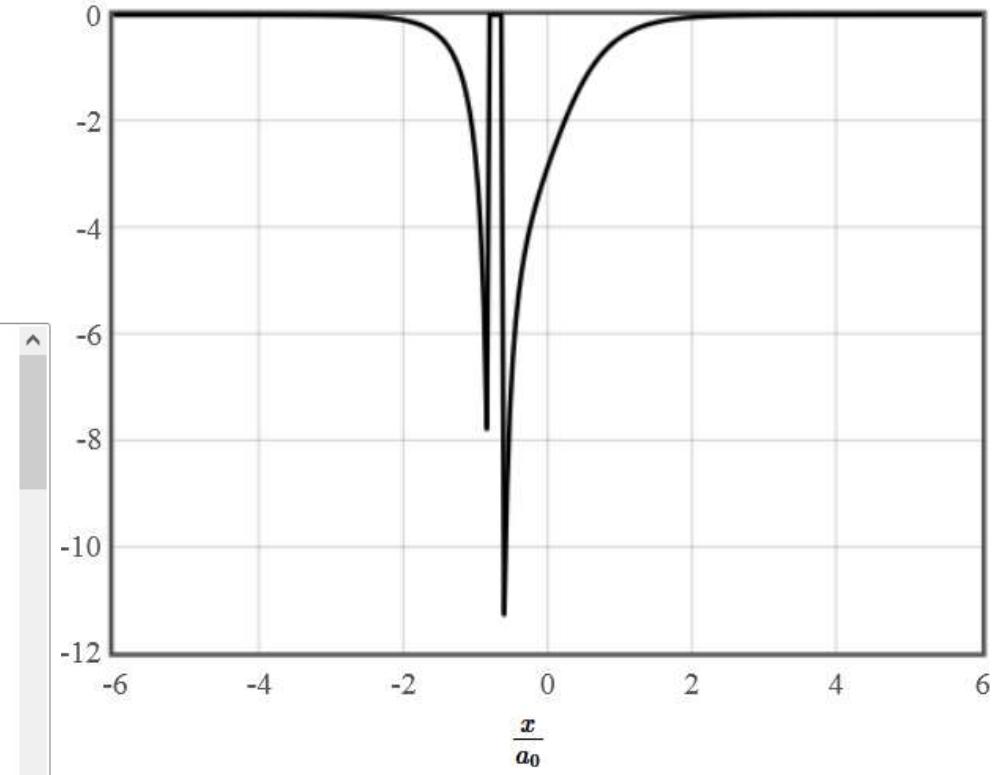
S12 = 0;
N = 1000000; //number of random points

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



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

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

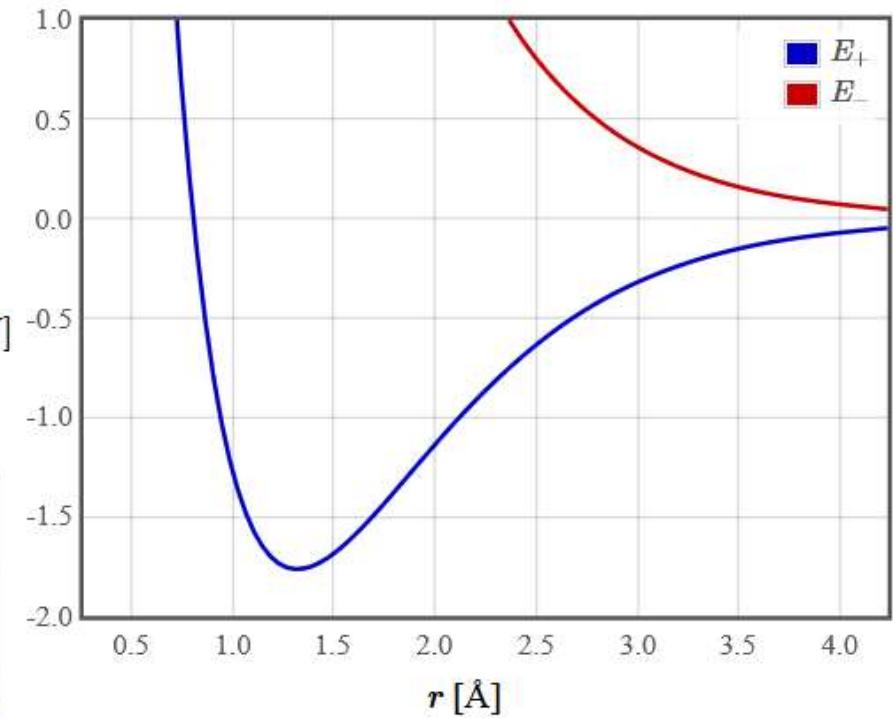
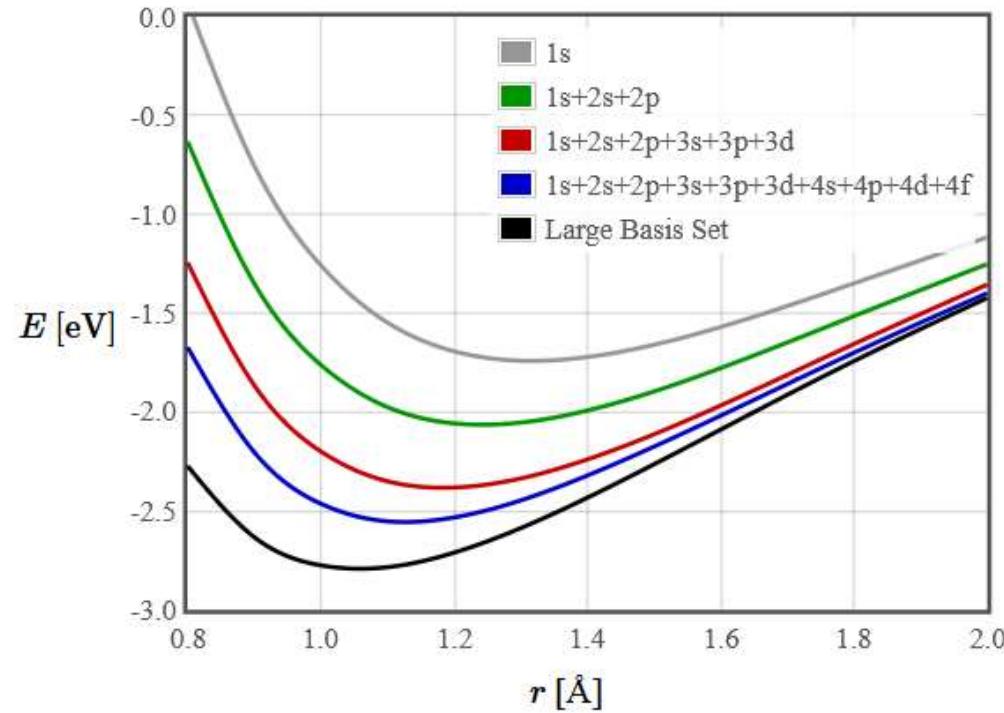


```
<script>
var a0 = 5.2917721E-11; // Bohr radius in meters
var pi = Math.PI;
var ec = 1.60217733E-19; //electron charge
var eps0 = 8.854187817E-12; //permittivity constant
var delta = a0/10;
var Zeff = 1; // effective nuclear
charge
var E1 = -Zeff*Zeff*2.17987e-18; // E1 in Joules
var x1 = -0.38E-10; // 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
  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_2^+ bond potential

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



Molecular orbitals of H₂

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

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

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

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

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

Molecular orbitals of H₂

