

# 3. Atoms / Molecules

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Mar. 10, 2020

# Exchange (Austauschwechselwirkung)

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$$\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1))$$

$$\begin{aligned} \langle \psi_A | H | \psi_A \rangle = & \frac{1}{2} [\langle \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) | H | \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \rangle - \langle \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) | H | \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \rangle \\ & - \langle \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) | H | \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \rangle + \langle \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) | H | \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \rangle] \end{aligned}$$

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$$\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_2)\phi_2(\vec{r}_1))$$

$$\begin{aligned} \langle \psi_S | H | \psi_S \rangle = & \frac{1}{2} [\langle \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) | H | \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \rangle + \langle \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) | H | \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \rangle \\ & + \langle \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) | H | \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \rangle + \langle \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) | H | \phi_1(\vec{r}_2)\phi_2(\vec{r}_1) \rangle] \end{aligned}$$

The difference in energy between the  $\psi_A$  and  $\psi_S$  is twice the **exchange energy**.

# Exchange

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The exchange energy can only be defined when you speak of multi-electron wavefunctions. It is the difference in energy between the symmetric solution and the antisymmetric solution. There is only a difference when the electron-electron term is included. Coulomb repulsion determines the exchange energy.

In ferromagnets, the antisymmetric state has a lower energy. Thus the state with parallel spins has lower energy.

In antiferromagnets, the symmetric state has a lower energy. Neighboring spins are antiparallel.

# Many electrons

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Consider a gold atom (79 electrons)

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

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

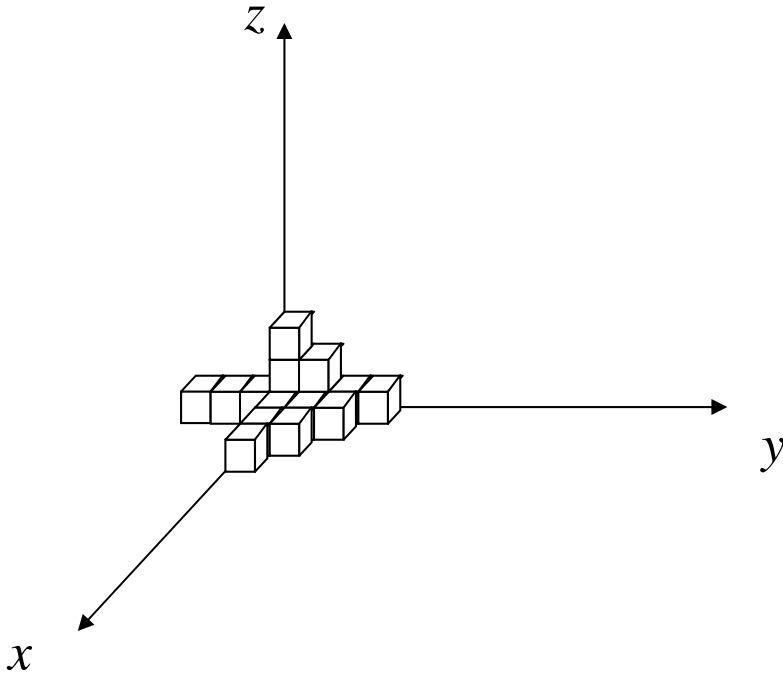
$\Psi(x_1, y_1, z_1, \dots, x_{79}, y_{79}, z_{79}, t)$  is a complex function in 237 dimensions

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

# Numerical solution of the Schrödinger equation for one electron

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

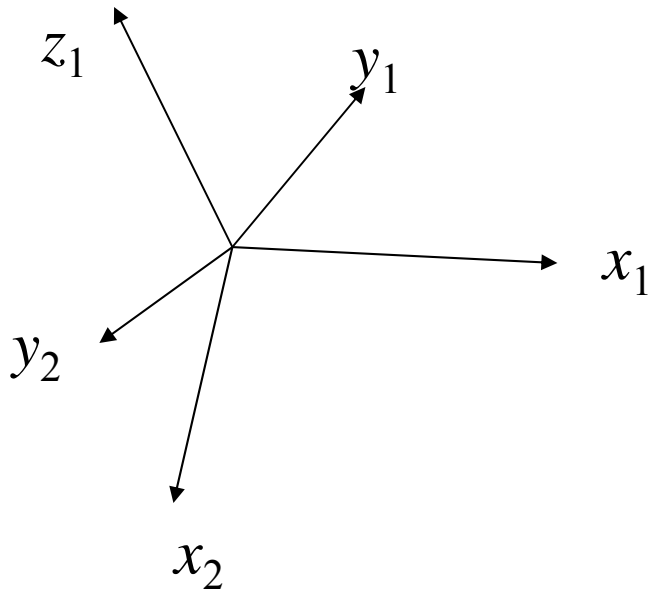


Discretize  $\Psi$  to solve numerically. For one electron  $\sim 10^6$  elements are needed.

# Numerical solution for many electrons

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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 % Programm zur numerischen Berechnung der zeitabhängigen Wellenfunktion eines Atoms mit Z Elektronen
clc % Programm funktioniert mit beliebiger Anzahl an Elektronen

Z = 1; % Ordnung-/Elektronen-/Protonenzahl des Atomes
e0 = 9.85418791762*10^ (0-12); % Permittivität
me = 9.10938291*10^ (0-31); % Elektronenmasse
h = 6.62606957*10^ (0-34); % planksches 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)); % Intervall zur numerischen Auswertung 2 Elemente weniger, da 2 beim Differenzenquotienten verloren gehen
I_1 = I(1:(end-2)); % Intervall zur numerischen Auswertung 2 Elemente weniger, da 2 beim Differenzenquotienten verloren gehen
I_2 = I(3:end); % Intervall zur numerischen Auswertung 2 Elemente weniger, da 2 beim Differenzenquotienten verloren gehen
Ik = [I;IO;I_1]; % alle 3 Intervalle werden in einer Matrix abgespeichert
t = [0:0.01:1]; % Intervall Zeit
dIndizes = 2:(numel(I)-1); % Vektor zur Indizierung für nicht betroffene x,y,z 1.Ableitung
dIndizes = 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;
    XO = repmat(reshape(IO,dimension),matrix); % 3Z dimensionale Matrix für jede Richtung; enthält Intervall für phi("x")
    matrix0(k) = XO; % abspeichern der Intervallmatrizen in eine Zeile, zum leichteren Auslesen
end

for k=1:(3.*Z)
    matrix=matrix0;
    for m=1:3
        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;
        XO = repmat(reshape(Ik(m,:),dimension),matrix); % 3Z dimensionale Matrix für jede Richtung; enthält Intervall für phi("x+dx/x-x-dx")
        matrix(k)=XO;
        phi = exp(0-sqrt(matrix(1).^2+matrix(2).^2+matrix(3).^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=0-2;
        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 d*phi/dx* = (phi(x+dx)-2*phi(x)+phi(x-dx))/(Schrittweite des Intervalles)
    end
end

for k=1:Z % Berechnung der Abstände Elektron-Kern + Summenbildung aller Terme
    rNE = (matrix0((k-1).*3+1).^2+matrix0((k-1).*3+2).^2+matrix0((k-1).*3+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:(Z-1) % Berechnung der Abstände Elektron-Elektron + Summenbildung aller Terme
    for m=2:Z
        rEE = ((matrix0((k-1).*3+1))-matrix0((m-1).*3+1)).^2+(matrix0((k-1).*3+2))-matrix0((m-1).*3+2)).^2+(matrix0((k-1).*3+3))-matrix0((m-1).*3+3)).^2;
        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)/(11) - (rNE_sum.*(2.*e.^2./(h.*2.*e0)).*phi0)/(11) - (h./(4.*pi.*me)).*ddphi_sum./(11); % Wellenfunktion d(phi)
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](http://lamp.tu-graz.ac.at/~hadley/ss1/studentpresentations/2011/n_electrons.m)

# Quantum computation

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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

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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](http://en.wikipedia.org/wiki/Many-body_problem)

# The Central Dilemma of Solid State Physics

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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.

# Neglect the e-e interactions

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Consider a gold atom (79 electrons)

$$\begin{aligned}
 &-\frac{\hbar^2}{2m} \left( \frac{d^2}{dx_1^2} \dots + \frac{d^2}{dz_{79}^2} \right) \Psi - \frac{79e^2}{4\pi\epsilon_0 r_j} \Psi \dots + \frac{e^2}{4\pi\epsilon_0 r_{ij}} \Psi \dots = E\Psi \\
 &\begin{array}{ccc}
 \nearrow & \nearrow & \nearrow \\
 3 \times 79 = 237 \text{ terms} & 79 \text{ terms} & \frac{79 \times 78}{2} = 3081 \text{ terms}
 \end{array}
 \end{aligned}$$

Out of desperation: We simplify the model for a solid until the Schrödinger can be solved. If the 3081 electron - electron terms are neglected, the equation can be solved exactly and the total wave function is a product of atomic orbitals.

This is called the **orbital approximation**.

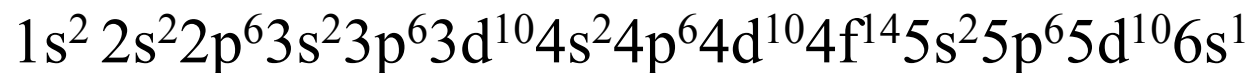
# Antisymmetrized product wave functions

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$$\begin{aligned}\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{79}) &= A \phi_{1s}^{Z_{eff}} \uparrow(\vec{r}_1) \phi_{1s}^{Z_{eff}} \downarrow(\vec{r}_2) \dots \phi_{6s}^{Z_{eff}} \uparrow(\vec{r}_{79}) \\ &= \left| \phi_{1s}^{Z_{eff}} \uparrow(\vec{r}_1) \phi_{1s}^{Z_{eff}} \downarrow(\vec{r}_2) \dots \phi_{6s}^{Z_{eff}} \uparrow(\vec{r}_{79}) \right>\end{aligned}$$

↖  
Dirac notation

The standard first approximation for the many-electron wave-function of any atom is an antisymmetrized product of atomic orbitals where  $Z$  is determined by Slater's rules.



# Electron configurations

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

# Orbital approximation

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- 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

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

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

# Filling of electron shells

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

You can evaluate the energy of any electron configuration.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{28}) = \left| \phi_{1s}^{28} \uparrow(\vec{r}_1), \phi_{1s}^{28} \downarrow(\vec{r}_2), \dots, \phi_{3d}^{28} \uparrow(\vec{r}_{27}), \phi_{4s}^{28} \uparrow(\vec{r}_{29}) \right\rangle$$

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

Hund's rules

# 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.

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

# Molecules

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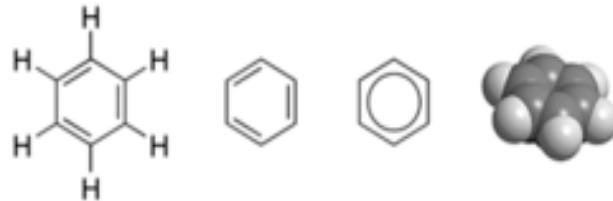
# The full Hamiltonian of a molecule

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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.

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

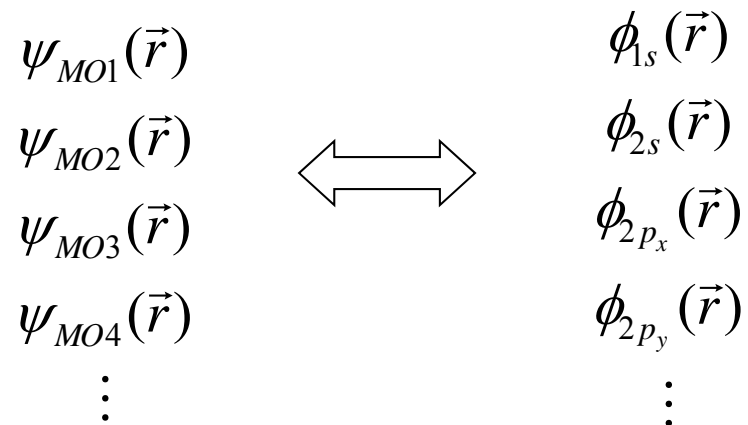
$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \cancel{\sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}$$

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

# Molecular 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.

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

# 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 with  $Z_{\text{eff}}$ .



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

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The 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.

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

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>

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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 H<sub>2</sub>

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

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

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

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

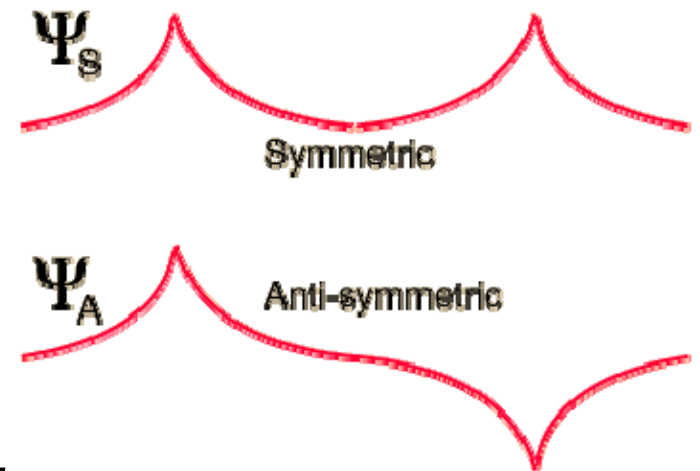
# Molecular orbitals of H<sub>2</sub>

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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 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)