

Many electron atoms

Many electrons

Consider a gold atom (79 electrons)

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

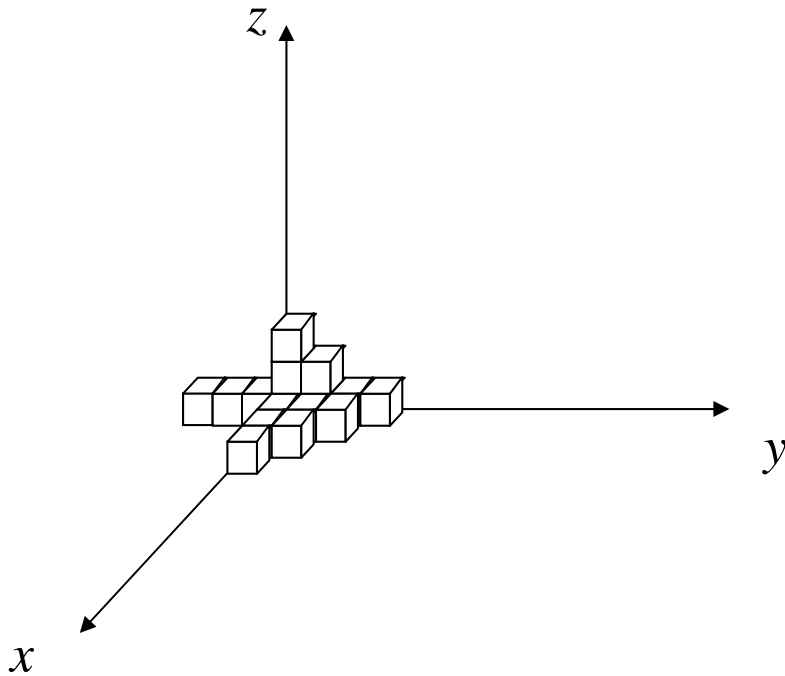
$3 \times 79 = 237$ terms 79 terms $\frac{79 \times 78}{2} = 3081$ terms

$\Psi(x_1, y_1, z_1, \dots, x_{79}, y_{79}, z_{79}, t)$ 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

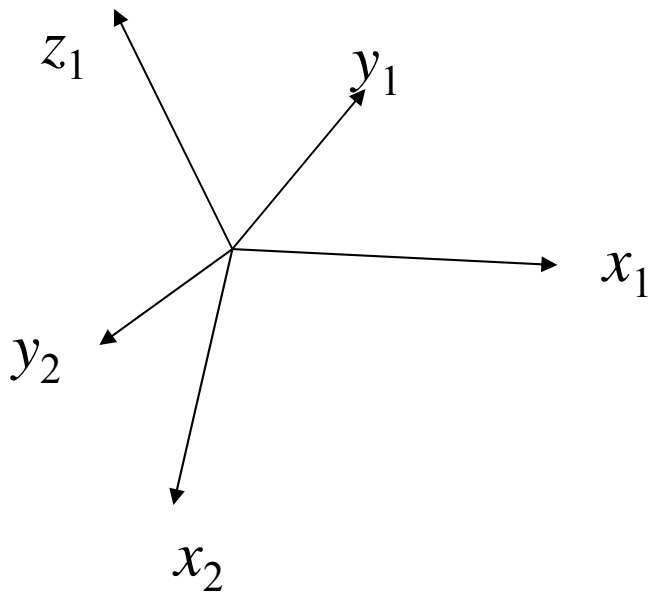
$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi - \frac{e^2}{4\pi\epsilon_0 r} \Psi$$



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 % 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^(-12); % Permittivität
me = 9.10938291*10^(-31); % Elektronenmasse
h = 6.62606957*10^(-34); % Plancksches Wirkungsquantum
e = 1.602176565*10^(-19); % Elementarladung
a0 = 0.52917721092*10^(-10); % Bohrscher Radius
I = [-1:0.02:1]*a0.*a0; % 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_2 = 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 32 Dimensionen
    matrix(k) = 1;
    XO = repmat(reshape(IO,dimension),matrix); % 32 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 32 Dimensionen
        matrix(k) = 1;
        XO = repmat(reshape(Ik(m,:),dimension),matrix); % 32 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.*a0).^2; % Summenbildung über d^2phi/dx^2 = (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
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

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

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	$1s^2 2s^2 2p^6 3s^2 3p^1$	$= [\text{Ne}] 3s^2 3p^1$
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	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	$= [\text{Ar}] 3d^{10} 4s^2$

Filling of electron shells



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

You can evaluate the energy of any electron configuration.

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

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

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.

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