

2. Atoms

March 8, 2018

Wave functions of hydrogen

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

Solve with the boundary condition $\Psi \rightarrow 0$ as $|\vec{r}| \rightarrow \infty$

Assume $\Psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi)$

Atomic orbitals

Z is the
number of
protons

$$\phi_{1s}^Z = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr}{a_0}},$$

$$\phi_{2s}^Z = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}},$$

$$\phi_{2px}^Z = \frac{1}{8} \sqrt{\frac{Z^3}{\pi a_0^3}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin \theta \cos \varphi,$$

$$\phi_{2py}^Z = \frac{1}{8} \sqrt{\frac{Z^3}{\pi a_0^3}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin \theta \sin \varphi,$$

$$\phi_{2pz}^Z = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi a_0^3}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \cos \theta,$$

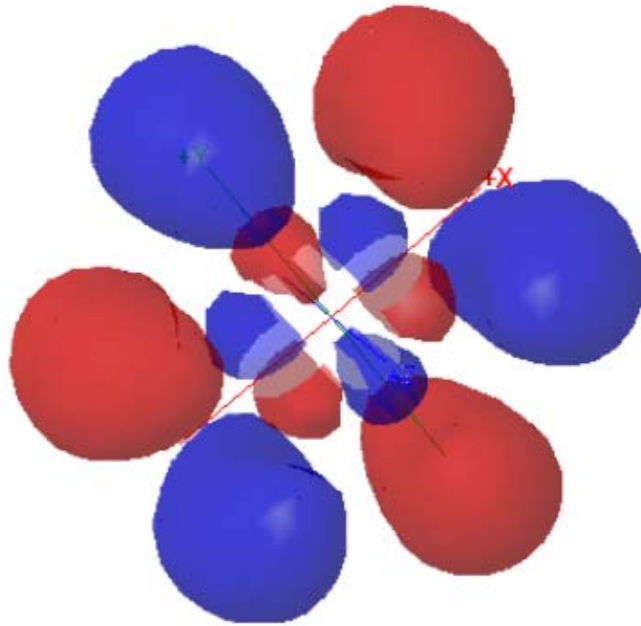
$$E = -\frac{Z^2 m e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{13.6 Z^2}{n^2} \text{ eV.}$$

Atomic orbitals

<http://lampx.tugraz.at/~hadley/ss1/molecules/atoms/AOs.php>

Atomic orbitals:

5f



1s								
2s						2px	2py	2pz
3s						3px	3py	3pz
4s	3d xy	3d yz	3d xz	3d z ²	3d x ² -y ²	4px	4py	4pz
5s	4d xy	4d yz	4d xz	4d z ²	4d x ² -y ²	5px	5py	5pz
6s	5d xy	5d yz	5d xz	5d z ²	5d x ² -y ²	6px	6py	6pz
	4f	4f	4f	4f	4f	4f		
	5f	5f	5f	5f	5f	5f		

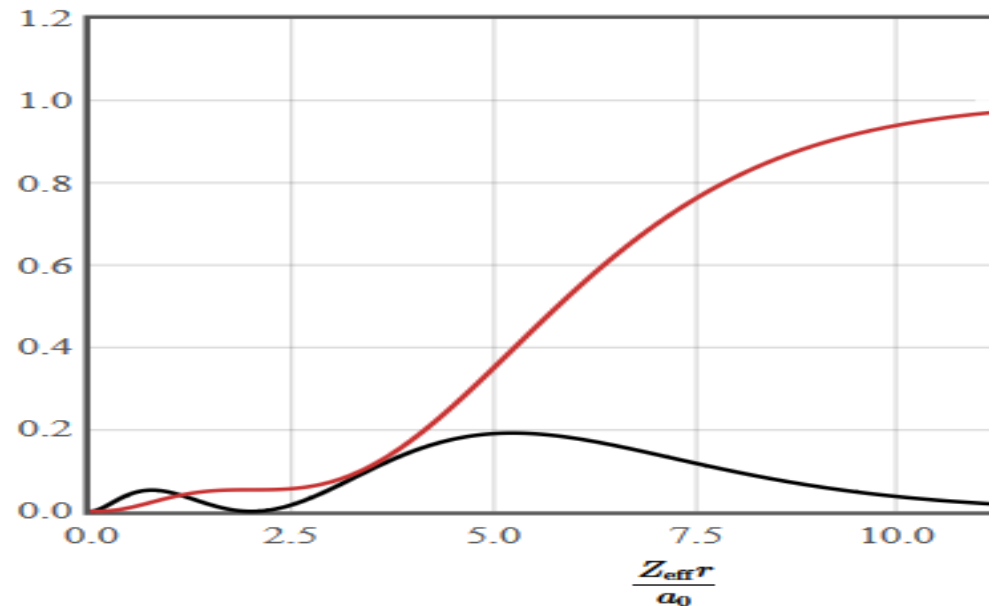
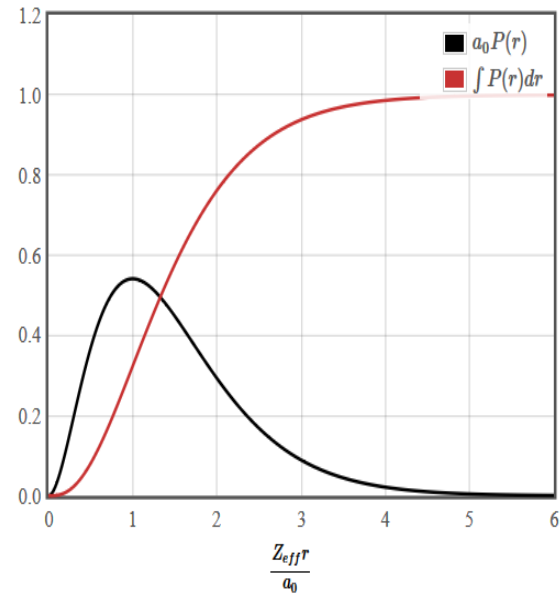
$$\langle \phi_m | H | \phi_n \rangle = \frac{-\hbar^2}{2m} \langle \phi_m | \nabla^2 \phi_n \rangle - \frac{2e^2}{4\pi\epsilon_0} \langle \phi_m | \frac{1}{|\vec{r}|} | \phi_n \rangle$$

Radial distribution function

$$P(r) = 4\pi r^2 |\Psi(r)|^2 dr$$

$$\phi_{1s}^Z = \sqrt{\frac{Z^3}{\pi a_0^3}} \exp\left(-\frac{Zr}{a_0}\right)$$

$$\phi_{2s}^Z = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$$



Approximate wavefunction

Often in molecular or solid state physics we know the Hamiltonian but we can't solve the Schrödinger equation associated with this Hamiltonian. In these cases we often guess a solution and then calculate the corresponding energy.

Consider the Hamiltonian for a hydrogen atom. In spherical coordinates it is,

$$H\Psi = \frac{-\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \Psi$$

Find the expectation value of the energy,

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

for the wavefunction

$$\Psi = \exp\left(\frac{-r^2}{a_0^2}\right)$$

Note that this wavefunction is not an eigenfunction of the Hamiltonian. Here $a_0 = 5.3 \times 10^{-11}$ m is the Bohr radius.

(You may use a computer algebra program to solve this problem.)

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\iiint \Psi^*(r, \theta, \varphi) H \Psi(r, \theta, \varphi) r^2 \sin \theta dr d\theta d\varphi}{\iiint \Psi^*(r, \theta, \varphi) \Psi(r, \theta, \varphi) r^2 \sin \theta dr d\theta d\varphi}$$

Helium atom

$$\frac{-\hbar^2}{2m} (\nabla_1^2 \Psi + \nabla_2^2 \Psi) - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} \Psi - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} \Psi + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \Psi = E\Psi$$

$|\Psi(\vec{r}_1, \vec{r}_2)|^2$ is the probability to find one of the electrons at r_1 and the other one at r_2 .

Helium atom

neglect the electron-electron interaction term

$$H_{red}^{He} = \frac{-\hbar^2}{2m} (\nabla_1^2 \Psi + \nabla_2^2 \Psi) - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} \Psi - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} \Psi + \cancel{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \Psi} = E\Psi$$

assume a product wave function

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi_1(\vec{r}_1) \phi_2(\vec{r}_2)$$

Separation of variables (Trennung der Veränderlichen)

$$\frac{-\hbar^2}{2m} \nabla_1^2 \phi_1 \phi_2 - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} \phi_1 \phi_2 = \frac{\hbar^2}{2m} \nabla_2^2 \phi_1 \phi_2 + \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} \phi_1 \phi_2 + E \phi_1 \phi_2$$

divide by $\phi_1 \phi_2$

$$\frac{-\hbar^2}{2m\phi_1} \nabla_1^2 \phi_1 - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} = C = \frac{\hbar^2}{2m\phi_2} \nabla_2^2 \phi_2 + \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} + E$$

$$\frac{-\hbar^2}{2m} \nabla_1^2 \phi_1 - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} \phi_1 = C \phi_1 \qquad \frac{-\hbar^2}{2m} \nabla_2^2 \phi_2 - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} \phi_2 = (E - C) \phi_2$$

Indistinguishable particles

$$|\Psi(\vec{r}_1, \vec{r}_2)|^2 = |\Psi(\vec{r}_2, \vec{r}_1)|^2$$

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

bosons

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

integer spin:
photons, phonons,
 ${}^4\text{He}$

fermions

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

half integer spin:
electrons, neutrons,
protons, ${}^3\text{He}$

Spin

Spin appears naturally in the relativistic formulation of quantum mechanics but in the nonrelativistic formulation, we just add the spins states.

\uparrow = spin up

\downarrow = spin down

Spin orbitals: $\phi_{1s} \uparrow, \phi_{1s} \downarrow, \phi_{2s} \uparrow, \phi_{2s} \downarrow, \dots$

Slater determinants

The antisymmetric N electron wave function can be written,

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

Exchanging two columns changes the sign of the determinant.

If two columns are the same, the determinant is zero = Pauli exclusion.

Dirac notation: $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = |\phi_{1s} \uparrow, \phi_{1s} \downarrow, \dots, \phi_N \uparrow\rangle$

Helium ground state

$$H_{total} = \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

Approximate antisymmetrized wave function (neglecting electron-electron interactions)

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

Energy neglecting
 $e-e$ interactions

$$\longrightarrow E = 2 \times \frac{-13.6Z^2}{n^2} = -108.8 \text{ eV}$$

Approximate ground state
evaluated with the total
Hamiltonian

$$\longrightarrow E = \frac{\langle \Psi | H_{total} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -74.83 \text{ eV}$$

Matrix elements

$$E_0^{\text{He}} \approx \frac{\langle \Psi_0^{\text{He}} | H_{\text{total}}^{\text{He}} | \Psi_0^{\text{He}} \rangle}{\langle \Psi_0^{\text{He}} | \Psi_0^{\text{He}} \rangle}$$

$$\frac{\iiint \iiint \Psi^*(x_1, y_1, z_1, x_2, y_2, z_2) H \Psi(x_1, y_1, z_1, x_2, y_2, z_2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2}{\iiint \iiint \Psi^*(x_1, y_1, z_1, x_2, y_2, z_2) \Psi(x_1, y_1, z_1, x_2, y_2, z_2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2}$$

Helium ground state

Try other wave functions in the full Hamiltonian

$$H_{total} = \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_1|} - \frac{2e^2}{4\pi\epsilon_0 |\vec{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \exp\left(\frac{-\alpha r_1}{a_0}\right) \exp\left(\frac{-\alpha r_2}{a_0}\right) \times (\text{polynomial in } r_1 \text{ and } r_2)$$

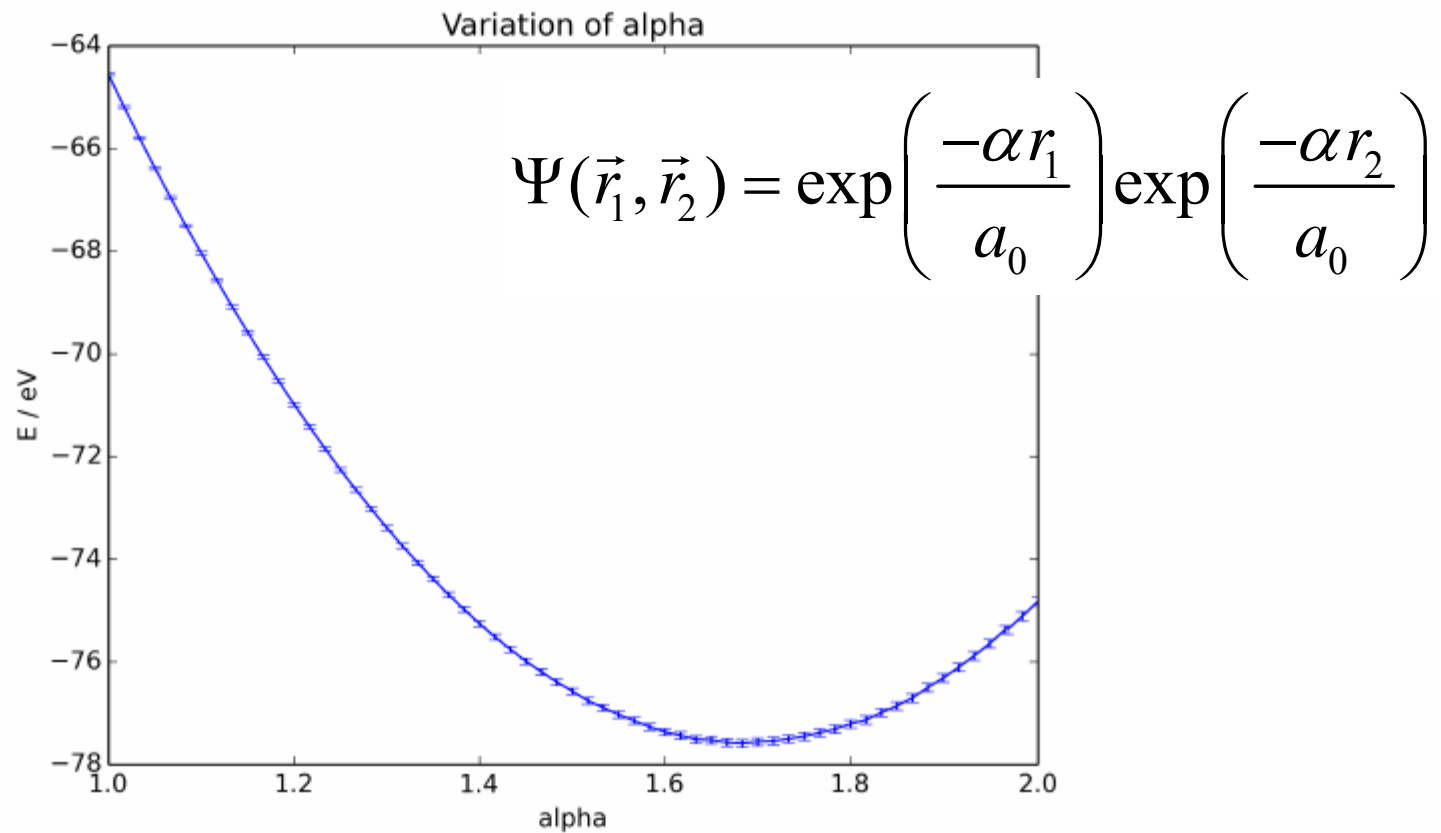
Electron screening makes the wave function larger

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

4.1 Helium

The results of the total energy of the helium ground state for different effective nuclear charges α are plotted in 1. The minimum (and therefore best estimate) lies at

$$\begin{aligned}\alpha &= (1.685 \pm 0.005) \\ E &= (-77.50 \pm 0.03) \text{ eV}\end{aligned}\tag{14}$$



Slater's rules

Effective Nuclear Charge Z_{eff}

	1s	2s,2p
H	1	
He	1.7	
Li	2.7	1.3
Be	3.7	1.95
B	4.7	2.6
C	5.7	3.25
N	6.7	3.9
O	7.7	4.55
Cl	8.7	5.2
Ne	9.7	5.85

Helium ground state

$e^{-2r_1} e^{-2r_2}$	-74.83 eV
$e^{-\alpha r_1} e^{-\alpha r_2}$	-77.4885 eV
$e^{-\alpha(r_1+r_2)} (1 + c \vec{r}_1 - \vec{r}_2)$	-78.6714 eV
1078 parameters	-79.0142 eV

The true wave function cannot be written as a product of two one-electron wave functions.

Helium excited states

One electron in 1s and one in 2s, $\uparrow\uparrow$, $\downarrow\downarrow$, $\downarrow\uparrow$, and $\uparrow\downarrow$

$$\Psi_I = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \uparrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \uparrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2)) \uparrow\uparrow,$$

$$\Psi_{II} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \downarrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \downarrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2)) \downarrow\downarrow,$$

$$\Psi_{III} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \uparrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \uparrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \downarrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{2s}^{\text{He}}(\vec{r}_2) \downarrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{1s}^{\text{He}}(\vec{r}_2) \uparrow),$$

$$\Psi_{IV} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\text{He}} \downarrow(\vec{r}_1) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_1) \\ \phi_{1s}^{\text{He}} \downarrow(\vec{r}_2) & \phi_{2s}^{\text{He}} \uparrow(\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{2s}^{\text{He}}(\vec{r}_2) \uparrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{1s}^{\text{He}}(\vec{r}_2) \downarrow).$$

$$E = \frac{\langle \Psi | H_{red}^{\text{He}} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -\frac{13.6 * 2^2}{1^2} - \frac{13.6 * 2^2}{2^2} = -68 \text{ eV}$$

The antisymmetric solution $\Psi = 0$ for $\vec{r}_1 = \vec{r}_2$.

Construct the Hamiltonian matrix

Schrödinger equation

$$H_{total}^{He} (c_I \Psi_I + c_{II} \Psi_{II} + c_{III} \Psi_{III} + c_{IV} \Psi_{IV}) = E (c_I \Psi_I + c_{II} \Psi_{II} + c_{III} \Psi_{III} + c_{IV} \Psi_{IV})$$

Multiply from left by Ψ_i .

$$\begin{bmatrix} H_{I,I} & H_{I,II} & H_{I,III} & H_{I,IV} \\ H_{II,I} & H_{II,II} & H_{II,III} & H_{II,IV} \\ H_{III,I} & H_{III,II} & H_{III,III} & H_{III,IV} \\ H_{IV,I} & H_{IV,II} & H_{IV,III} & H_{IV,IV} \end{bmatrix} \begin{bmatrix} c_I \\ c_{II} \\ c_{III} \\ c_{IV} \end{bmatrix} = E \begin{bmatrix} c_I \\ c_{II} \\ c_{III} \\ c_{IV} \end{bmatrix}$$

$$H_{i,j} = \langle \Psi_i | H_{total}^{He} | \Psi_j \rangle$$

Student project: determine this matrix

Transform to symmetric and antisymmetric orbital solutions

$$\Psi_I = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2)) \uparrow\uparrow,$$

$$\Psi_{II} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2)) \downarrow\downarrow,$$

$$\Psi_{III} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{2s}^{\text{He}}(\vec{r}_2) \downarrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{1s}^{\text{He}}(\vec{r}_2) \uparrow),$$

$$\Psi_{IV} = \frac{1}{\sqrt{2}} (\phi_{1s}^{\text{He}}(\vec{r}_1) \downarrow \phi_{2s}^{\text{He}}(\vec{r}_2) \uparrow - \phi_{2s}^{\text{He}}(\vec{r}_1) \uparrow \phi_{1s}^{\text{He}}(\vec{r}_2) \downarrow).$$

$$\Psi_V = \frac{1}{\sqrt{2}} (\Psi_{III} + \Psi_{IV}) = \frac{1}{2} ((\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) - \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2))(\uparrow\downarrow + \downarrow\uparrow),$$

$$\Psi_{VI} = \frac{1}{\sqrt{2}} (\Psi_{III} - \Psi_{IV}) = \frac{1}{2} ((\phi_{1s}^{\text{He}}(\vec{r}_1)\phi_{2s}^{\text{He}}(\vec{r}_2) + \phi_{2s}^{\text{He}}(\vec{r}_1)\phi_{1s}^{\text{He}}(\vec{r}_2))(\uparrow\downarrow - \downarrow\uparrow).$$

Helium excited states

$H_{\text{red}}^{\text{He}}$	$H_{\text{total}}^{\text{He}}$	exact
	<u>$1s^1 2s^1$ -55.98 eV</u>	<u>$1s^1 2s^1$ 2^1S -58.37 eV singlet</u>
	$1s^1 2s^1$ -58.19 eV	$1s^1 2s^1$ 2^1S -59.16 eV triplet
<u>$1s^1 2s^1$ -68 eV</u>		
	<u>$1s^2$ -77.49 eV</u>	<u>$1s^2$ 1^1S -78.99 eV singlet</u>
<u>$1s^2$ -108.8 eV</u>		

$$\frac{-13.6Z^2}{n^2} \text{ eV}$$

Energy Levels of Neutral Helium (He I)



Basic Atomic Spectroscopic Data

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¹ H																	² He
³ Li	⁴ Be											⁵ B	⁶ C	⁷ N	⁸ O	⁹ F	¹⁰ Ne
¹¹ Na	¹² Mg											¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar
¹⁹ K	²⁰ Ca	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu	³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se	³⁵ Br	³⁶ Kr
³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
⁵⁵ Cs	⁵⁶ Ba	*	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn
⁸⁷ Fr	⁸⁸ Ra	+															
* Lanthanides			⁵⁷ La	⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu
+ Actinides			⁸⁹ Ac	⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es				

$$E = hf = hc/\lambda$$

Names refer to approximate solutions

Configuration	Term	J	Level (cm ⁻¹)	Ref.
1s ²	1s	0	0.000	M02
1s2s	3s	1	159855.9745	M02
1s2s	1s	0	166277.4403	M02
1s2p	3p°	2	169086.7666	M02
		1	169086.8430	M02
		0	169087.8309	M02
1s2p	1p°	1	171134.8970	M02
1s3s	3s	1	183236.7918	M02
1s3s	1s	0	184864.8294	M02
1s3p	3p°	2	185564.5620	M02
		1	185564.5840	M02
		0	185564.8547	M02
1s3d	3D	3	186101.5463	M02
		2	186101.5488	M02
		1	186101.5930	M02
1s3d	1D	2	186104.9668	M02
1s3p	1p°	1	186209.3651	M02
1s4p	1p°	1	191492.7120	M02
He II (2s _{1/2})	Limit		198310.6691	M02

Exchange (Austauschwechselwirkung)

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

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

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

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

The difference in energy between the ψ_A and ψ_S is twice the **exchange energy**.

Exchange

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

Consider a gold atom (79 electrons)

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

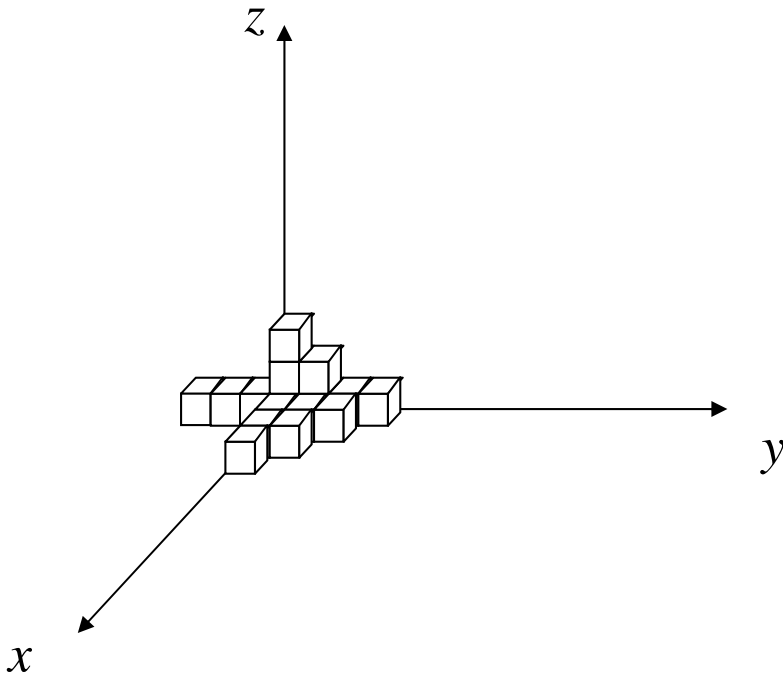
$3 \times 79 = 237$ terms 79 terms $\frac{79 \times 78}{2} = 3081$ terms

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

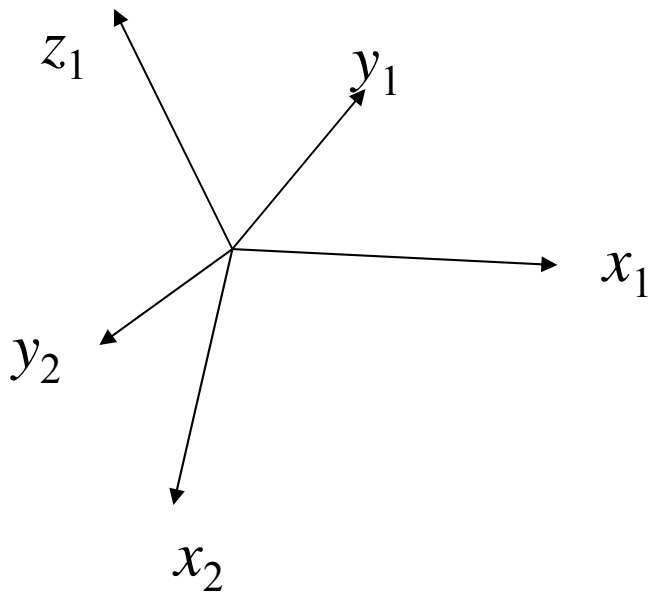
$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi - \frac{e^2}{4\pi\epsilon_0 r} \Psi$$



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; % 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 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.*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.

Neglect the e-e interactions

Consider a gold atom (79 electrons)

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

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.

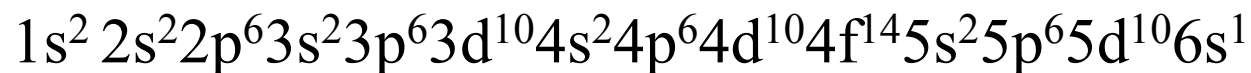
This is called the **orbital approximation**.

Antisymmetrized product wave functions

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

↖
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

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

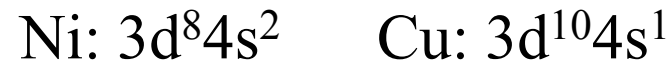
Orbital approximation

- 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



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

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

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.

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