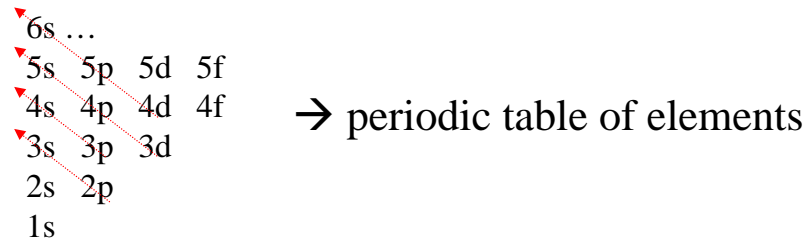


3.2) Many-electron systems ¹¹⁰

- electrons occupy states with different combinations of n, ℓ, m, s
- filling sequence determined by interplay between $V_{eff}(r)$ and centrifugal potential $\propto \ell(\ell+1)/r^2$



- state with lowest energy found using Hund's rules:
 - 1) filled (sub-) shells have total angular momentum $L = 0$, $S = 0$
 - 2) state with maximum S (parallel spins) are occupied first
 - 3) state with maximum L compatible with S
 - 4) for more than half-filled subshells $J = L + S$, else $J = |L - S|$

- ad 1) $\vec{L} = \sum \vec{\ell}_i = 0$; $\vec{S} = \sum \vec{s}_i = 0$ 111
 direct consequence of Pauli principle: if a shell is filled, there must be an equal number of electrons with positive and negative spin orientations $\rightarrow J = L + S = 0$
- ad 2) wavefunctions must be antisymmetric (Pauli principle)
 \rightarrow wavefunction with symmetric spin part (maximum S) has antisymmetric orbital wavefunction \rightarrow maximum "distance" between electrons \rightarrow minimum Coulomb repulsion
- ad 3) \rightarrow state of first electron in new shell has $|m_\ell| = \ell$, then state with $|m_\ell| = \ell - 1$ is filled ...
 explanation: average distance from the core increases with increasing $m_\ell \rightarrow$ larger average distance between electrons \rightarrow smaller Coulomb repulsion (effect smaller than for rule 2)
- ad 4) rules 2 and 3 determine S and $L \rightarrow$ possible values for J range from $|L - S|$ to $L + S$; half-filled shells: $L = 0$ (rule 3) $\rightarrow J = S$
 magnetic properties of atoms determined by J

periodic table of elements (1869): Dmitri Mendelejew (1834–1907)
Lothar Meyer (1830–1895)

similarities of chemical properties → horizontal grouping
1864: hypothesis of inner structure of atoms

Periodensystem nach Lothar Meyer (1870)

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	<u>B</u> =11,0	<u>Al</u> =27,3	—	—	—	? <u>In</u> =113,4	<u>Tl</u> =202,7	—
	<u>C</u> =11,97	<u>Si</u> =28	—	—	—	<u>Sn</u> =117,8	—	<u>Pb</u> =206,4
	<u>N</u> =14,01	<u>P</u> =30,9	<u>Ti</u> =48	—	<u>Zr</u> =89,7	<u>Sb</u> =122,1	—	<u>Bi</u> =207,5
	<u>Q</u> =15,96	<u>S</u> =31,98	<u>V</u> =51,2	<u>As</u> =74,9	<u>Nb</u> =93,7	<u>Te</u> =128?	<u>Ta</u> =182,2	—
—	<u>E</u> =19,1	<u>Cl</u> =35,8	<u>Cr</u> =52,4	<u>Se</u> =78	<u>Mo</u> =95,6	<u>I</u> =126,5	<u>W</u> =183,5	—
			<u>Mn</u> =54,8	<u>Br</u> =79,75	<u>Ru</u> =103,5	—	<u>Os</u> =198,6?	—
			<u>Fe</u> =55,9	—	<u>Rh</u> =104,1	—	<u>Ir</u> =196,7	—
			<u>Co</u> = <u>Ni</u> =58,6	—	<u>Pd</u> =106,2	—	<u>Pt</u> =196,7	—
<u>Li</u> =7,01	<u>Na</u> =22,99	<u>K</u> =39,04	—	<u>Rb</u> =85,2	—	<u>Cs</u> =132,7	—	—
			<u>Cu</u> =63,3	—	<u>Aq</u> =107,66	—	<u>Au</u> =196,2	—
? <u>Be</u> =9,3	<u>Mg</u> =23,9	<u>Ca</u> =39,9	—	<u>Sr</u> =87,0	—	<u>Ba</u> =136,8	—	—
			<u>Zn</u> =64,9	—	<u>Cd</u> =111,6	—	<u>Hg</u> =199,8	—

Quelle: Annalen der Chemie, Supplementband 7, 354 (1870)

periodic table of elements (1869): Dmitri Mendelejew (1834–1907)
Lothar Meyer (1830–1895)

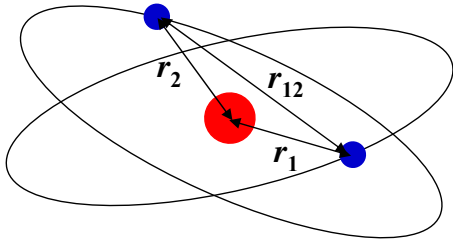
electronic configuration of outer shell determines
chemical properties → vertical grouping

Reihen	Gruppe I. $\overline{R^2O}$	Gruppe II. \overline{RO}	Gruppe III. $\overline{R^2O^3}$	Gruppe IV. $\overline{RH^4}$ $\overline{RO^2}$	Gruppe V. $\overline{RH^3}$ $\overline{R^2O^5}$	Gruppe VI. $\overline{RH^2}$ $\overline{RO^3}$	Gruppe VII. \overline{RH} $\overline{R^2O^7}$	Gruppe VIII. $\overline{RO^4}$
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	—	—	—	Th=231	—	U=240	—	—

Mendelejew: *Die periodische Gesetzmäßigkeit der Elemente*

Annalen der Chemie und Pharmacie. VIII. Supplementband 1871, S. 133-229

the helium atom – two electrons in the field of the nucleus



$$H = \left(-\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \right) =$$

$$= \left(\underbrace{H^{(1)}(r_1)}_{\text{one-electron Hamiltonian}} + \underbrace{H^{(1)}(r_2)}_{\text{one-electron Hamiltonian}} + \underbrace{V^{(2)}(r_{12})}_{\text{interaction potential}} \right)$$

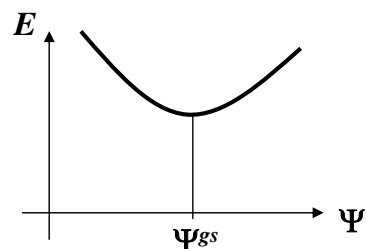
generalization to N electrons:

$$\left\{ \underbrace{-\frac{1}{2} \sum_i \nabla_i^2}_{T^{(1)}} - \sum_i \underbrace{\frac{Ze^2}{|\vec{r}_i|}}_{V_{ne}^{(1)}} + \sum_{i < j} \underbrace{\frac{1}{|\vec{r}_i - \vec{r}_j|}}_{V_{ee}^{(2)}} - E \right\} \Psi(\vec{r}_1, \dots, \vec{r}_N) = 0$$

Schrödinger equation cannot be solved analytically

ground state has minimum energy:

$$\rightarrow E[\Psi^{gs} + \Delta\Psi] > E[\Psi^{gs}]$$



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\rightarrow ground state can be found by variation of Ψ until $E = E_{min}$

$$\min_{\Psi}(E) = \min \langle \Psi | H | \Psi \rangle = \min \langle \Psi | T^{(1)} + V_{ne}^{(1)} + V_{ee}^{(2)} | \Psi \rangle$$

constraints:

- wavefunction remains normalized
- electrons obey Pauli exclusion principle, i.e.,
wavefunction changes sign upon particle interchange

$$\Psi(r_1, \dots, \underbrace{r_i, \dots, r_j}_{\text{interchange}}, \dots, r_N) = -\Psi(r_1, \dots, \underbrace{r_j, \dots, r_i}_{\text{interchange}}, \dots, r_N)$$

\rightarrow two electrons: parallel spins \rightarrow antisymmetric orbital WF
antiparallel spins \rightarrow symmetric orbital WF

ansatz: product wavefunctions (Hartree)

$$\Psi = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \dots \psi_N(\vec{r}_N)$$

(would be exact for non-interacting electrons)

$$\min_{\Psi} (E) = \min \langle \Psi | T^{(1)} + V_{ne}^{(1)} + V_{ee}^{(2)} | \Psi \rangle$$

→ e.g. helium atom:

electrostatic potential

$$\left(-\frac{\hbar}{2m} \Delta_1 - \frac{2}{r_1} + \int \frac{1}{r_{12}} \psi_2^2(\vec{r}_2) d^3 r_2 \right) \psi_1(\vec{r}_1) = E_1 \psi_1(\vec{r}_1)$$

$$\left(-\frac{\hbar}{2m} \Delta_2 - \frac{2}{r_2} + \int \frac{1}{r_{12}} \psi_1^2(\vec{r}_1) d^3 r_1 \right) \psi_2(\vec{r}_2) = E_2 \psi_2(\vec{r}_2)$$

to minimize: $E = E_1 + E_2 - \iint \frac{1}{r_{12}} \psi_1^2(\vec{r}_1) \psi_2^2(\vec{r}_2) d^3 r_1 d^3 r_2$

self-consistency loop:

$$\psi_i^0 \rightarrow H^0, E^0 \rightarrow \psi_i^1 \rightarrow H^1, E^1 \rightarrow \dots \rightarrow \psi_i^{gs}, \Psi^{gs}, E^{gs}$$

antisymmetrized product-wavefunction (Hartree-Fock)

Slater determinant for $\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \dots & \psi_1(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\vec{r}_1) & \dots & \psi_N(\vec{r}_N) \end{vmatrix}$

interaction potential in Hamiltonian contains “exchange” term

minimization: $E_{HF}^{gs} = \min_{\Psi} \langle \Psi | H | \Psi \rangle$

$$H |\psi_i\rangle = \left(-\frac{1}{2} \nabla^2 + V_{ne} + V_{ee}[\psi] \right) |\psi_i\rangle = \varepsilon_i |\psi_i\rangle$$

side remark: only for closed shell systems can the wavefunction be represented by single determinant → wavefunction is linear combination of Slater determinants (“multi-configuration HF”, “multi-reference configuration interaction”)

example: helium $\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) \\ \psi_1(r_2) & \psi_2(r_2) \end{vmatrix}_{\pm} \cdot \chi(s_1, s_2)$

$$\rightarrow \langle \Psi | H | \Psi \rangle = \langle \Psi | H(1) + H(2) + \underbrace{W(12)}_{e^2/r_{12}} | \Psi \rangle$$

$$\langle \Psi | W(12) | \Psi \rangle \rightarrow V_{Coul} = e^2 \int \frac{|\psi_1(r_1)|^2 |\psi_2(r_2)|^2}{r_{12}} d^3 r_1 d^3 r_2 \text{ (Coulomb-term)}$$

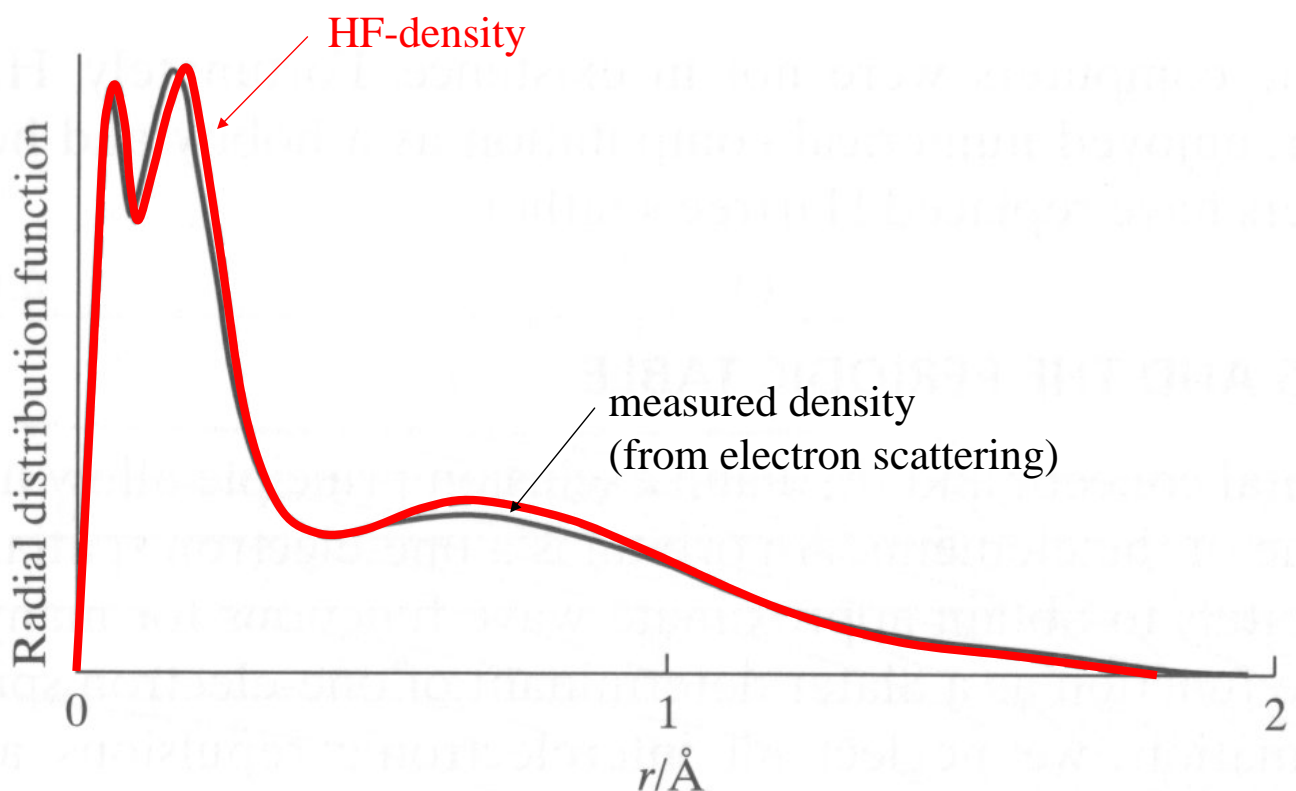
$$V_{ex} = e^2 \int \frac{\psi_1^*(r_1) \psi_2(r_1) \psi_1(r_2) \psi_2^*(r_2)}{r_{12}} d^3 r_1 d^3 r_2 \text{ (exchange term)}$$

states with lowest energy:

spins antiparallel, $S = 0$ (singlet) \rightarrow symmetric orbital wavefunction ($1s^2$)
energy $E_{sing} = 2E_1 + V_{Coul} + V_{ex}$

spins parallel, $S = 1$ (triplet) \rightarrow antisymmetric orbital wavefunction ($1s2s$)
energy $E_{trip} = E_1 + E_2 + V_{Coul} - V_{ex} > E_{sing}$

radial Hartree-Fock density of Ar 121



Thomas-Fermi model (1927)

write energy as an approximate function(al) of the density

$$E = E[n] = T_{TF}[n] + \underbrace{\int V_{ne}(\vec{r})n(\vec{r})d^3r + \frac{1}{2} \iint \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2}_{\int V_{es}[n(\vec{r})]n(\vec{r})d^3r}$$

many electrons \rightarrow classical approximation (see electron gas):
number of electrons N determines maximum momentum

$$\begin{aligned} p_{\max}^3 = 3n\pi^2 &\rightarrow \langle T[n] \rangle = \frac{3}{5} T_{\max}[n] = \frac{3}{5} \frac{(3\pi^2 n)^{2/3}}{2m} \\ &\rightarrow T_{TF}[n] = \frac{3}{10m} (3\pi^2)^{2/3} \int n^{5/3}(\vec{r}) d^3r \end{aligned}$$

good approximation for large atoms at intermediate distances r

maximum density at $r \sim \frac{a_0}{Z^{1/3}}$; half of electrons within $r < \frac{4a_0}{3Z^{1/3}}$

density-functional theory (1964; Nobel prize 1998)

Hohenberg-Kohn: knowledge of ground-state density sufficient
to calculate observable ground-state properties

density from Schrödinger wavefunction:

$$n(\vec{r}) = \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2, \dots, d\vec{r}_N = n[\Psi]$$

\rightarrow information compression $\mathbb{R}^{3N} \rightarrow \mathbb{R}^3$

Hohenberg-Kohn theorem I:

every observable can be expressed as functional of density

$$\langle \Psi_{gs} | O | \Psi_{gs} \rangle = O[\Psi_{gs}] = O[n_{gs}]$$

Hohenberg-Kohn theorem II:

unique mapping between ground state wavefunction and density

$$\rightarrow E_{gs}[n_{gs}] = E_{gs}[\Psi_{gs}]$$

Kohn-Sham (1965):

recipe to implement DFT: construct a system of non-interacting pseudo-particles which give the correct ground-state density

$$n(\vec{r}) = \sum_i |\varphi_i(\vec{r})|^2$$

→ Kohn-Sham equations

$$\left\{ -\frac{1}{2} \nabla^2 + \underbrace{V_{\text{ext}}[n(\vec{r})] + V_{\text{es}}[n(\vec{r})] + V_{\text{xc}}[n(\vec{r})]}_{V_{\text{eff}}[n(\vec{r})]} \right\} \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

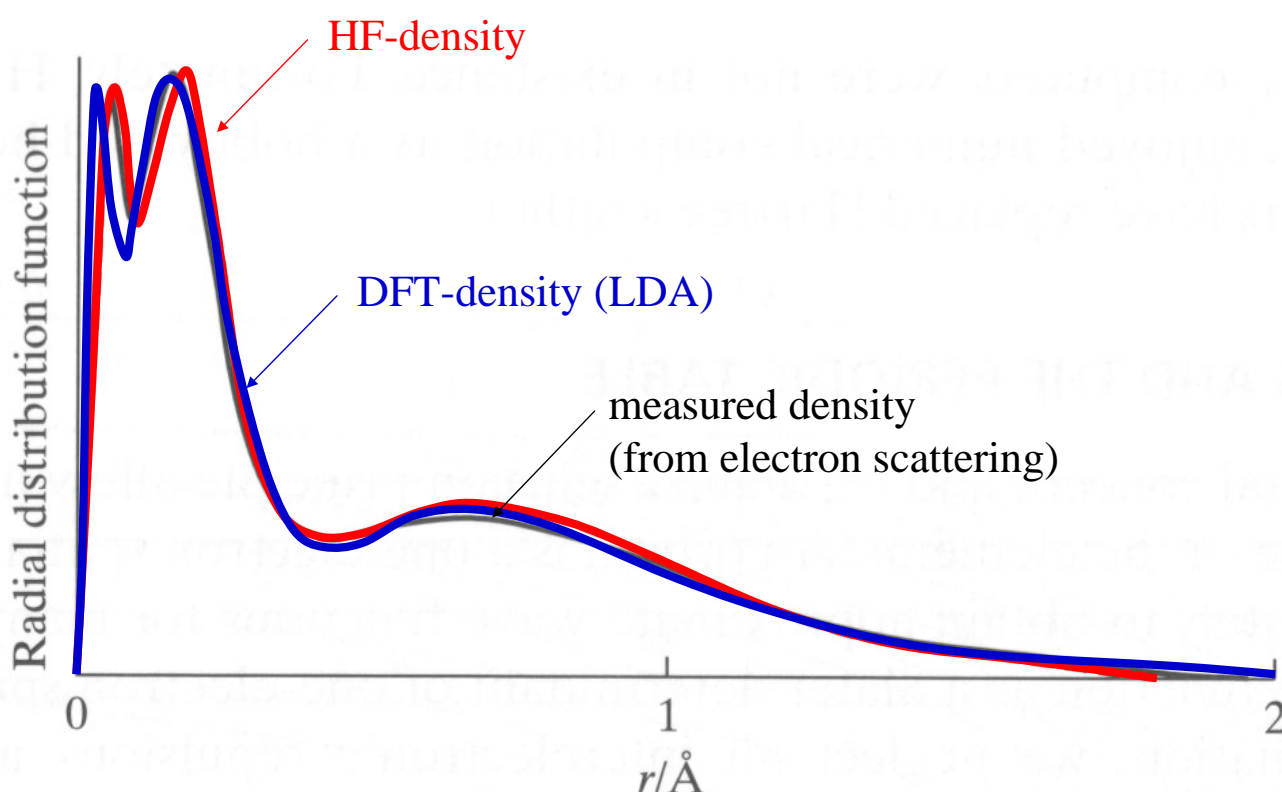
interaction potential including exchange and correlation

φ_i **DO NOT** represent orbitals of particles

iterative solution: $n_0(\vec{r}) \rightarrow V_{\text{eff}}[n_0] \rightarrow \varphi_i[n_0] \rightarrow n_1(\vec{r}) \rightarrow \dots \rightarrow n_{\text{gs}}(\vec{r})$

advantage: numerical effort reduced

disadvantage: V_{xc} unknown

radial DFT density of Ar

DFT density of large systems¹²⁶

e.g., electron density at metal surfaces:

define a unit cell (“supercell”), containing many atomic and a thick vacuum layers; periodic boundary conditions

→ “crystal” made of thin metal slabs

