02/02/2021

Multielectron atom and periodic table

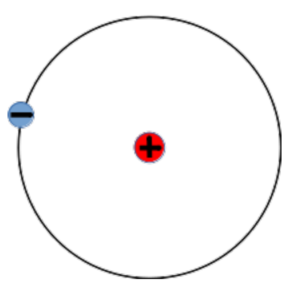
a) A concept of multialectron atom & periodic table

b) Helium atom

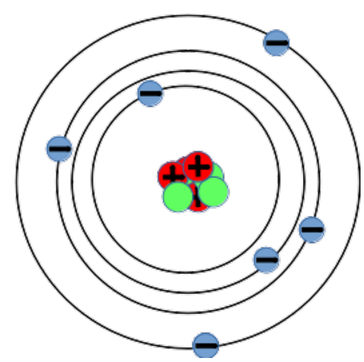
c) Hartree and Hartree-Fock methods

Part a

Hydrogen atom



Multielectron atom



Hamiltonian

$$H = \boxed{\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i}\right)} + \boxed{\sum_{i<j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}$$

The relevant quantum numbers

n – principal quantum number $n = 1, 2, 3, \ldots$

l – the orbital angular momentum quantum number $l = 0, 1, 2, \ldots, n-1$

m_l – the magnetic quantum number $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

m_s – the spin quantum number $m_s = \pm \frac{1}{2}$

n	l	Degeneracy	N
1	0	2	2
2	0,1	$2 \times (1+3) = 8$	$2+8=10$
3	0,1,2	$2 \times (1+3+5) = 18$	$2+10+18=28$
4	0,1,2,3	$2 \times (1+3+5+7) = 32$	$2+8+18+32=60$

$\uparrow\downarrow$

$l=0\ (\uparrow\downarrow)\quad l=1$

$m_l = -1, 0, 1$

$\uparrow\downarrow\quad \uparrow\downarrow\quad \uparrow\downarrow$

At the magic numbers Z=2,10,28,60... the atoms will have a full shell of electrons

The notation of configuration

$n\,\#^{\ell}$

↑principal q.n.

$\# = (s, p, d, \ldots \text{etc})$

$l = 0, 1, 3, \ldots$

$\ell \rightarrow$ is the number of electrons in these states

The electrons which have the same value of n are said to sit in the same shell.

Electrons that have the same value of n and l are said to sit in the same sub-shell.

Each sub-shell contains 2(l + 1) different states.

Electrons which sit in fully filled shells (or sometimes sub-shells) are said to be part of the core electrons.

Those which sit in partially filled shells are said to form the valence electrons.

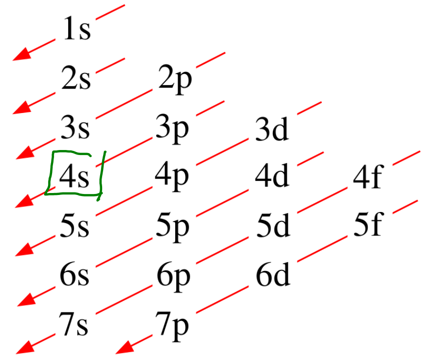
Electron configuration in atomic ground states

1. Pauli exclusion principle

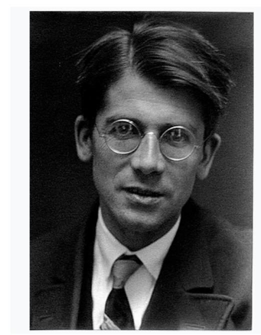
those atomic states exist in such any two electrons differ in at least one of the 4 their quantum number

2. The aufbau principle (formulated by Bohr and Pauli in 1920s)

It says the state 1s, 2s, 2p, 3s, 3p, 4s, 3d....



3. Hund's rule (by Friedrich Hund, 1925)



$\uparrow \uparrow \uparrow$

→ for electrons having the same l they are placed in such configuration in which the total spin S is maximal

→ if S is maximized then electrons are distributed in such a way to maximize L_z

→ $J = L + S$

Examples of configuration & periodic table

Z	1	2
Element	H	He
Electrons	$1s^1$	$1s^2$

$1s^1$ $1s^2$

$\uparrow$ $\uparrow\downarrow$

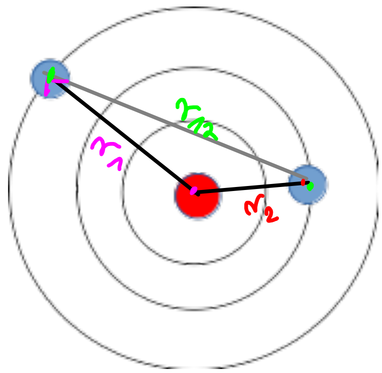
Z	3	4	5	6	7	8	9	10
	Li	Be	B	C	N	O	F	Ne
[He]+	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$

Z	11	12	13	14	15	16	17	18
	Na	Mg	Al	Si	P	S	Cl	Ar
[Ne]+	$3s^1$	$3s^2$	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^6$	$3s^23p^6$

Why do the electrons prefer to first fill up the 2s states, followed by 2p states?

Z	19	20	21	22	...	30	31	...	36
	K	Ca	Sc	Ti	...	Zn	Ga	...	Kr
[Ar]+	$4s^1$	$4s^2$	$3d^14s^2$	$3d^24s^2$	...	$3d^{10}4s^2$	$3d^{10}4s^24p^1$	...	$3d^{10}4s^24p^6$

Part b: Helium atom



Hamiltonian for two electrons orbiting a nucleus

$$H = \frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_1} + \frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

$|x_1 - x_2| = r_{12}$

The ground state Both electrons sit in 1s state

$n = 1$, $l = 0$, $m_l = 0$ $\qquad \uparrow\downarrow$ $n = 1$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1,0,0}(\mathbf{r}_1)\psi_{1,0,0}(\mathbf{r}_2)$$

$$\boxed{\psi_{1,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0}}$$

$$|0,0\rangle = \frac{|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}$$

$|\psi\rangle_H = |\psi(r_1, r_2)\rangle \otimes |0,0\rangle$

within variational method $\qquad$ Z-variational parameter

$$Z = 2 - \frac{5}{16}$$

"screening"

$E_{V_0} \approx -77.5\,\text{eV}$ $\qquad$ $E_0 \approx -79\,\text{eV}$

The first excited states

Non-interacting model ---

$\underbrace{1s^1 \overbrace{2s^1}}$

$1s^1 \to (1,0,0) \doteq (n, l, m_l)$

$2s^1 \to (2,0,0)$

$\underbrace{1s^1 2p^1}$

$1s^1 \to (1,0,0)$

$2p^1 \to (2,1,m_l)$ $\quad m_l = 0, \pm 1$

Hints:
- the Hamiltonian is blind to the spin degrees of freedom-- the wavefunction is a tensor product of a spatial state with a spin state

-electrons are fermions-- the wavefunction must be anti-symmetric under exchange of the two particles

- the symmetric spatial wave-function and the anti-symmetric spin wavefunction, or vice versa

spatial wave function

$$\Psi_{ab\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)\right)$$

$a\, b \to$ $\quad a = (1,0,0) \quad b = (2,0,0) \quad 1s^1 2s^1$

$\quad a = (1,0,0) \quad b = (2,1,m_l) \quad 1s^1 2p^1$

"+" symmetric

"-" anti-symmetric

singlet or triplet for spin degrees of freedom

$\to$ $|0,0\rangle = \frac{|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}}$ antisymmetric

$\to$ $|1,1\rangle = |\uparrow\rangle|\uparrow\rangle \quad , \quad |1,0\rangle = \frac{|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle}{\sqrt{2}} \quad , \quad |1,-1\rangle = |\downarrow\rangle|\downarrow\rangle$

symmetric

$|\psi\rangle_H = |\psi_{ab+}(r_1, r_2)\rangle \otimes |0,0\rangle$ $\quad$ 4 states

$|\psi\rangle_H = |\psi_{ab-}(r_1, r_2)\rangle \otimes \begin{cases} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \end{cases}$ $\quad 4 \times 3 = 12$ states

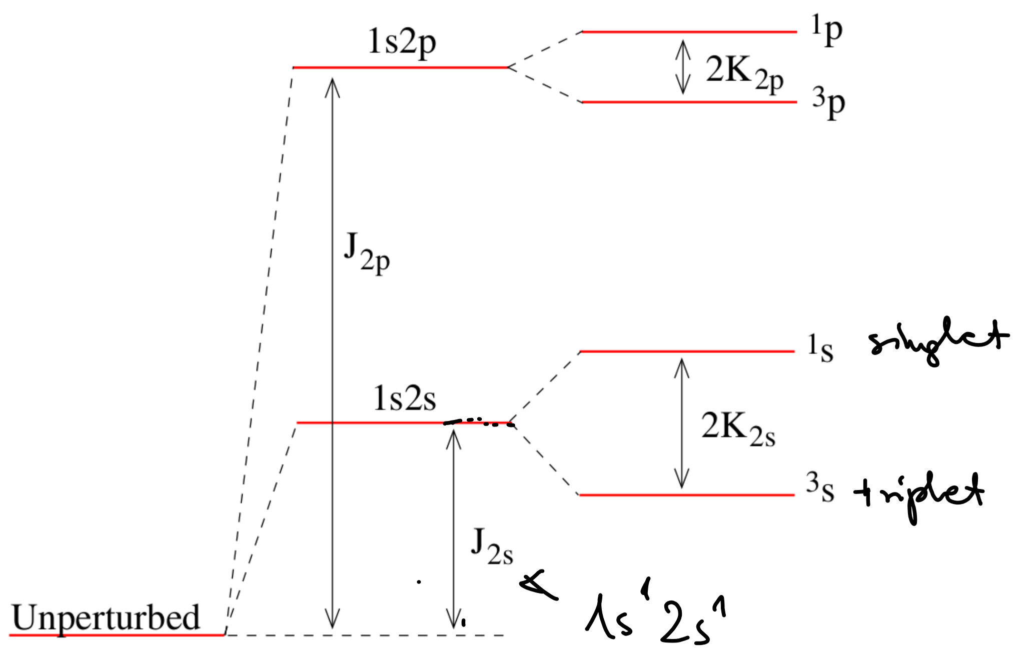
<Hint>

$$\Delta E_{ab\pm} = \frac{1}{4\pi\epsilon_0}\int d^3r_1 d^3r_2\ \frac{|\Psi_{ab\pm}(\mathbf{r}_1,\mathbf{r}_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|} = J_{ab} \pm K_{ab}$$

$$J_{ab} = \frac{1}{4\pi\epsilon_0}\int d^3r_1 d^3r_2\ \frac{|\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|} > 0$$

the spin-triplet states have lower energy!

$$K_{ab} = \frac{1}{4\pi\epsilon_0}\int d^3r_1 d^3r_2\ \frac{\psi_a^\star(\mathbf{r}_1)\psi_b^\star(\mathbf{r}_2)\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|} > 0$$



Comments:

The first excited states of helium sit in both spin-singlets and spin-triplets.

Transitions between these two states can only occur through the two photons emission.

The lifetime of the 1s2s state is around 2.2 hours (the longest lived of all excited states of neutral atoms)

Before these transitions were observed, it was thought that there were two different kinds of helium atoms: those corresponding to spin-singlet states (parahelium) and those corresponding to spin-triplets (orthohelium)

Part c: the self-consistent field method

A variational approach to multi-electron atoms where the concept of screening is taken into account

The Hartree method

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_{a_1}(\mathbf{r}_1)\,\psi_{a_2}(\mathbf{r}_2)\ldots\psi_{a_N}(\mathbf{r}_N) \qquad\qquad a = (n, l, m)$$

The multi-electron Hamiltonian

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i}\right) + \sum_{i<j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The average energy

$$\langle E\rangle = \sum_{i=1}^{N}\int d^3r\ \psi^\star_{a_i}(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\right)\psi_{a_i}(\mathbf{r})$$
$$+\frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\int d^3r\,d^3r'\ \frac{\psi^\star_{a_i}(\mathbf{r})\,\psi^\star_{a_j}(\mathbf{r}')\,\psi_{a_i}(\mathbf{r})\,\psi_{a_j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

direct integral

To enforce normatization of individual wave-functions

$$F[\Psi] = \langle E\rangle - \sum_i \epsilon_i\left(\int d^3r\ |\psi_{a_i}(\mathbf{r})|^2 - 1\right) \qquad\qquad \frac{\delta F[\Psi]}{\delta\psi_{a_i}(\mathbf{r})} = 0$$

Hartree equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\int d^3r'\ \frac{|\psi_{a_j}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}}_{U_{a_i}(r)}\right]\psi_{a_i}(\mathbf{r}) = \epsilon_i\psi_{a_i}(\mathbf{r})$$

N-equations

Numerical, self-consistent solution of the Schrödinger equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} + U_{a_i}(r)\right]\psi_{a_i}(\mathbf{r}) = \epsilon_i \psi_{a_i}(\mathbf{r})$$

The Hartree-Fock method

A repeat of the Hartree method, but now with the fully anti-symmetrised wavefunction

$$|\Psi\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} |\psi_{a_1}(1)\rangle & |\psi_{a_1}(2)\rangle & \dots & |\psi_{a_1}(N)\rangle \\ |\psi_{a_2}(1)\rangle & |\psi_{a_2}(2)\rangle & \dots & |\psi_{a_2}(N)\rangle \\ \vdots & & \ddots & \\ |\psi_{a_N}(1)\rangle & |\psi_{a_N}(2)\rangle & \dots & |\psi_{a_N}(N)\rangle \end{vmatrix}$$

Slater determinant

$\psi_{a_1}(1)$

$$\begin{aligned}\langle E\rangle = &\sum_{i=1}^{N}\int d^3r\ \psi^\star_{a_i}(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\right)\psi_{a_i}(\mathbf{r}) \\ &+\frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\int d^3r\, d^3r'\ \frac{\psi^\star_{a_i}(\mathbf{r})\,\psi^\star_{a_j}(\mathbf{r}')\,\psi_{a_i}(\mathbf{r})\,\psi_{a_j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &-\frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\int d^3r\, d^3r'\ \frac{\psi^\star_{a_i}(\mathbf{r})\,\psi^\star_{a_j}(\mathbf{r}')\,\psi_{a_i}(\mathbf{r}')\,\psi_{a_j}(\mathbf{r})\boxed{\delta_{m_{si},m_{sj}}}}{|\mathbf{r}-\mathbf{r}'|}\end{aligned}$$

Comments:

- the delta function means that the exchange term lowers the energy only when spins are aligned (one of Hund's rules) $\uparrow\ \uparrow\ \uparrow$

- when we start to fill a shell, the exchange term means that it's preferable for all the spins to point in the same direction

- the next electron to go in after half-filling should have a noticeably larger energy and the atom will, correspondingly, have a smaller ionization energy

The Hartree-Fock equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} + U(\mathbf{r})\right]\psi_{a_i}(\mathbf{r}) - \int d^3r'\; U^{\mathrm{ex}}_{a_i}(\mathbf{r},\mathbf{r}')\psi_{a_i}(\mathbf{r}') = \epsilon_i\psi_{a_i}(\mathbf{r})$$

$$U(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\int d^3r'\;\frac{|\psi_{a_j}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

$$U^{\mathrm{ex}}_{a_i}(\mathbf{r},\mathbf{r}') = \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\int d^3r'\;\frac{\psi^{\star}_{a_j}(\mathbf{r}')\,\psi_{a_j}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\delta_{m_{si},m_{sj}}$$

Final remarks:

- solved numerically in the self-consistent way

- the presence of the exchange term makes even numerical solutions considerably harder

-this scheme has some success in reproducing the properties of atoms observed in the periodic table, in particular the aufbau principle and Hund's rule