PAULI PRINCIPLE and He ATOM (p. 288-290 Levine)

We now reconsider the He atom from the standpoint of the electronic spin and the Pauli principle

In the orbital approximation used to build wave functions of polielectronic atoms (example of He), we have written the wave function for the ground state as a product of mono-electronic functions, such as $1s(1)1s(2)$. However, this function violates the antisymmetry Pauli principle. We must then consider the electronic spin. To take the spin into account, we must **multiply the spatial eigenfunction by a spin eigenfunction**. We shall use the notation $\alpha(1)\beta(2)$ to indicate a state where electron 1 has spin up and electron 2 has spin down. Since each electron has 2 possible spin states, we have at first sight 4 possible spin functions

$$\alpha(1)\alpha(2) \qquad \beta(1)\beta(2) \qquad \alpha(1)\beta(2) \qquad \alpha(2)\beta(1)$$

PAULI PRINCIPLE and He ATOM (p. 288-290 Levine)

$$\alpha(1)\alpha(2) \qquad \beta(1)\beta(2) \qquad \alpha(1)\beta(2) \qquad \alpha(2)\beta(1)$$

There is nothing wrong with the first two functions (they consider the **electrons as indistinguishable**). So, in principle we can build wave functions multiplying the spatial eigenfunction by the spin function

$$1s(1)1s(2)\,\alpha(1)\,\alpha(2) \qquad 1s(1)1s(2)\,\beta(1)\,\beta(2)$$

Instead, the functions with $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$ violate the principle of indistinguishability of electrons. For example, considering the spin function $\alpha(1)\beta(2)$, we can write

$$1s(1)1s(2)\,\alpha(1)\,\beta(2)$$

Upon exchange of the electrons, we get neither symmetric nor antisymmetric wave functions

$$1s(2)1s(1)\,\alpha(2)\,\beta(1)$$

PAULI PRINCIPLE and He ATOM

(p. 288-290 Levine)

$$\alpha(1)\alpha(2) \qquad \beta(1)\beta(2) \qquad \alpha(1)\beta(2) \qquad \alpha(2)\beta(1)$$

Intuition suggests that instead of $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$, we can use the following normalized combinations

$$\frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)] \qquad \frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

So we have 4 possibilities

Symmetric functions

$$\alpha(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]$$

Antisymmetric function

$$\frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

PAULI PRINCIPLE and He ATOM (p. 288-290 Levine)

We now include the spin in the spatial wave function of He. The function $1s(1)1s(2)$ is symmetric with respect to the exchange of the 2 electrons. According to the Pauli principle, the overall wave functions, including spin, must be antisymmetric with respect to the exchange of 2 arbitrary electrons. Therefore, we must **multiply the symmetric space function by an antisymmetric spin function**. There is only one antisymmetric two-electron spin function. This implies that the wave function for the He atom including spin is

$$\psi(1,2) = \frac{1}{\sqrt{2}} 1s(1)1s(2)\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

To a very good approximation, the Hamiltonian does not contain spin terms, so that the energy is unaffected by inclusion of the spin factor in the wave function

SLATER DETERMINANTS (p. 294-296 Levine)

For He-like atoms we have seen

$$\psi(1,2) = \frac{1}{\sqrt{2}} 1s(1)1s(2)\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

which has been built starting from the product of H-like orbitals, $1s(1)1s(2)$, and devising a special combination of spin functions

How to build antisymmetric wave functions in a systematic way?

We start from functions involving both space and spin variables

$$f(1) = 1s(1)\,\alpha(1)$$

A function like $f(1)$ is called **spin-orbital**. A spin-orbital is the product of a one-electron spatial orbital and a one-electron spin function

SLATER DETERMINANTS (p. 294-296 Levine)

Spin-orbitals are employed to build a special determant called **Slater determinant**

$$\psi(1,2,\ldots,n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} f_1(1) & f_2(1) & \ldots & f_n(1) \\ f_1(2) & f_2(2) & \ldots & f_n(2) \\ \ldots & \ldots & \ldots & \ldots \\ f_1(n) & f_2(n) & \ldots & f_n(n) \end{vmatrix}$$

All the elements in a given column of a Slater determinant involve the same spin-orbital f_i, whereas elements in the same row all involve the same electron. The factor $1/\sqrt{n!}$ is the normalization factor

Factorial

$$n! = n(n-1)(n-2)\cdots 3\ 2\ 1$$

SLATER DETERMINANTS (p. 294-296 Levine)

We now see the He atom

$$\psi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

$$\psi(1,2) = \frac{1}{\sqrt{2}} 1s(1)1s(2)\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$$

This is the result that we obtained before

SLATER DETERMINANTS (p. 294-296 Levine)

What happens if the same spin-orbital is used more than one time in the Slater determinant?

$$\psi(1,2,\dots,n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} f_1(1) & f_1(1) & \dots & f_n(1) \\ f_1(2) & f_1(2) & \dots & f_n(2) \\ \dots & \dots & \dots & \dots \\ f_1(n) & f_1(n) & \dots & f_n(n) \end{vmatrix} = 0$$

The determinat is ZERO!
This is physically unacceptable

In the columns of a Slater determinant, we cannot use a spin-orbital more than one time

SLATER DETERMINANTS (p. 294-296 Levine)

Pauli exclusion principle: **No two electrons can occupy the same spin-orbital.** Another way of stating this is to say that **no two electrons in an atom can have the same values for all their quantum numbers**.

The Pauli exclusion principle is a consequence of the more general Pauli-principle antisymmetry requirement

SLATER DETERMINANTS (p. 294-296 Levine)

Other faster ways to write a Slater determinant

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix}$$

$$\psi(1,2,3) = |1s \quad \overline{1s} \quad 2s|$$

POLIELECTRONIC ATOMS

The spin-orbitals used to build the wave functions of polielectronic atoms (using the Slater determinant) are those with lowest energy

So, for He atom $\psi(1,2) = |1s\ \overline{1s}|$

has lower energy than $\psi(1,2) = |1s\ \overline{2s}|$

… and also lower than $\psi(1,2) = |1s\ 2p_x|$

Because $1s$ has lower energy than $2s$ and $2p_x$

POLIELECTRONIC ATOMS

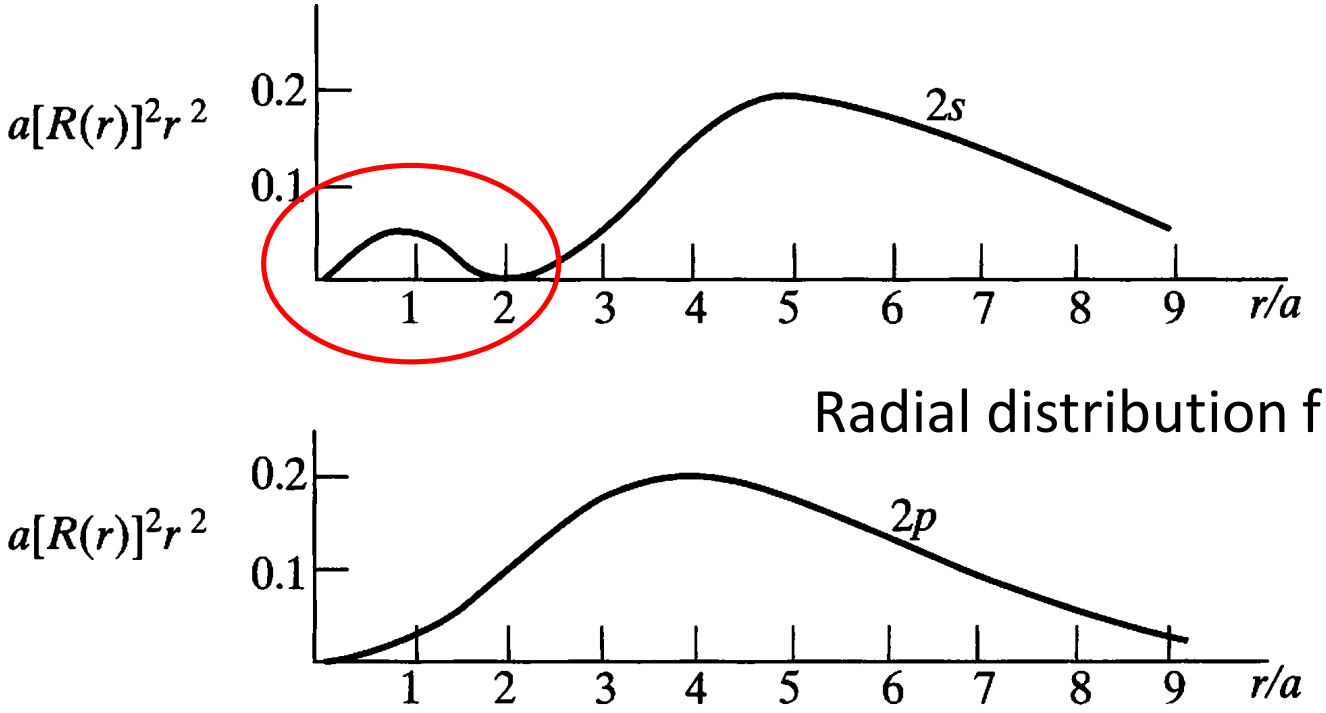
What happens for Li? Which of the following wave functions has lower energy?

$$\psi(1,2,3) = |1s\ \overline{1s}\ 2s| \quad \text{or} \quad \psi(1,2,3) = |1s\ \overline{1s}\ 2p_x|$$

If we consider the energy of hydrogen-like orbitals, we note that $2s$ and $2p_x$ are degenerate because their energies depend only on n (principal quantum number). So, the 2 wave functions would have the same energy

$$E = -\frac{Z^2 e'^2}{2\,a\,n^2} \qquad \text{For Li} \qquad \begin{matrix} Z = 3 \\ n = 2 \end{matrix}$$

POLIELECTRONIC ATOMS



Radial distribution functions

We see that the orbital $2s$ has a electronic density closest to the nucleus with respect to a generic $2p$ orbital (electronic density represented by the red circle).

This implies that **the electron in the $2p$ orbital is shielded by the electron in the $2s$ orbital**

POLIELECTRONIC ATOMS

The shielding effect implies that the electron in the $2p$ orbital «feels» a smaller nuclear charge. This smaller nuclear charge is called **effective nuclear charge, Z_{eff}**

$$Z_{eff} = Z - s$$

Shielding constant

$s > 0$ Because it should lead to a decrease of nuclear charge

$s < 1$ Because the maximum screeining occurs, in principle, if the $2s$ electron is located on the nucleus (or better, if the $2s$ electron is totally internal with respect to the $2p$ electron)

The effect of the shielding constant on the $2s$ and $2p$ energies is

$$E_{2s} = -\frac{Z^2 e'^2}{2\,a\,n^2} \qquad E_{2p} = -\frac{Z_{eff}^2 e'^2}{2\,a\,n^2}$$

POLIELECTRONIC ATOMS

Since $0 < s < 1$, we have

$$E_{2p} - E_{2s} = \frac{e'^2\, s(2Z - s)}{2\, a\, n^2} > 0$$

and hence $E_{2p} > E_{2s}$

Degenercy for orbitals s and p of the same shell (n) disappears

Since the radial distribution function is the same for $2p_x$, $2p_y$ and $2p_z$, the electrons located in these orbitals feel the same effective nuclear charge, Z_{eff} (the $2s$ electrons act in the same way on the 3 orbitals). This means that $2p$ orbitals are degenerate

To be precise, the $1s$ electrons are more internal than $2s$ and $2p$ so that Z_{eff} for $2s$ and $2p$ is lowered further (but lowering is the same)

POLIELECTRONIC ATOMS

The same reasoning holds for:

- $3s$ and $3p$, so that $E_{3p} > E_{3s}$
- $3p$ and $3d$, so that $E_{3d} > E_{3p}$

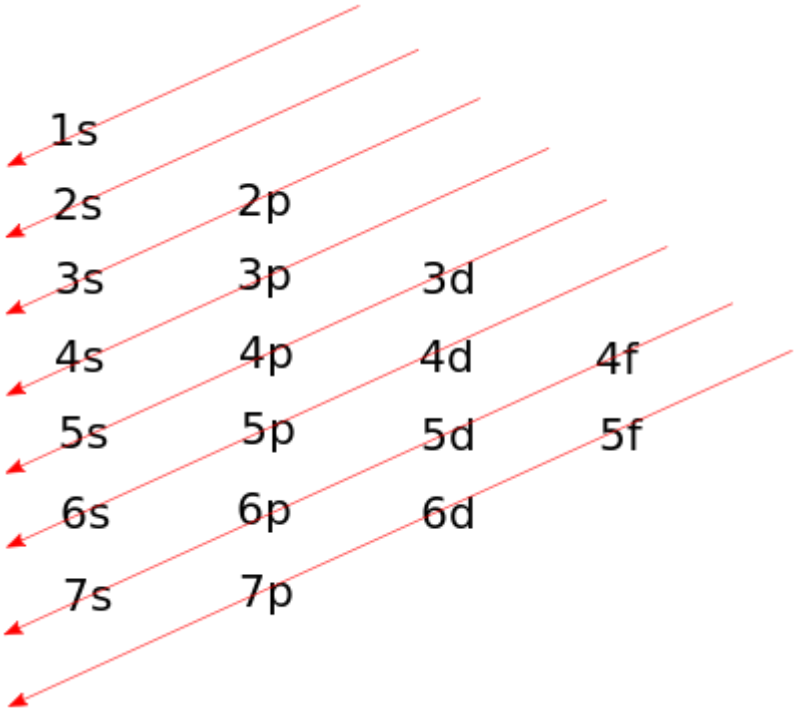
In general $\boxed{E_{nf} > E_{nd} > E_{np} > E_{ns}}$

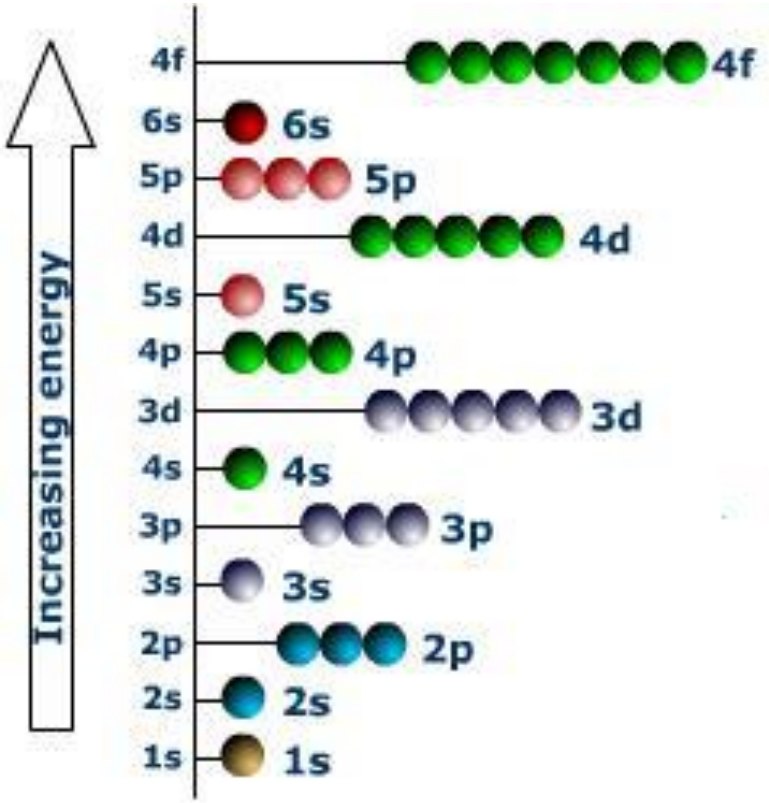
n is the principal quantum number

Thus the energy depends not only on the principal quantum number (n), but also on the secondary quantum number (l)

POLIELECTRONIC ATOMS

The filling order of the atomic orbitals is





POLIELECTRONIC ATOMS

At the moment, according to the **energy order** and **Pauli exclusion principle**, the wave functions for polielectronic atoms are

Li $\psi(1,2,3) = |1s\ \overline{1s}\ 2s|$ or $\psi(1,2,3) = |1s\ \overline{1s}\ \ \overline{2s}|$

Be $\psi(1,2,3,4) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}|$

B $\psi(1,2,3,4,5) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x|$

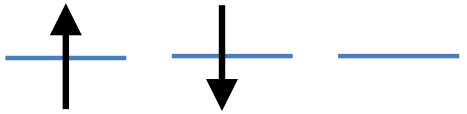
Other degenerate wave functions are possible

POLIELECTRONIC ATOMS

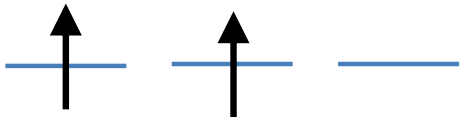
What happens to carbon? Possibilities are the following

$$\psi_a(1,2,3,4,5,6) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\ \overline{2p_x}|$$

$$\psi_b(1,2,3,4,5,6) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\ \overline{2p_y}|$$



$$\psi_c(1,2,3,4,5,6) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\ 2p_y|$$



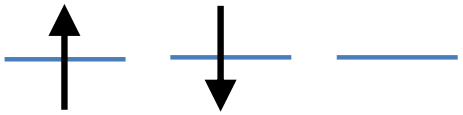
Other $2p$ orbitals can be considered. However, the electronic spin configurations reported above represent all possible different spin combinations

POLIELECTRONIC ATOMS

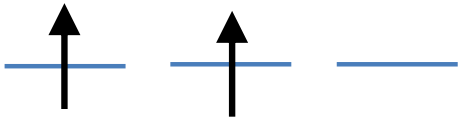
To simplify the discussion, suppose we have 2 electrons to be displaced in degenerate orbitals, such as $2p_x$, $2p_y$ and $2p_z$. The wave function of this hypotetical atom can be

$$\psi_a(1,2) = |2p_x\ \overline{2p_x}|$$

$$\psi_b(1,2) = |\ 2p_x\ \overline{2p_y}|$$



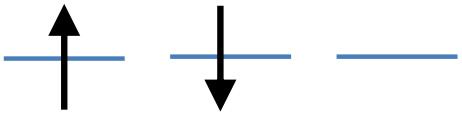
$$\psi_c(1,2) = |\ 2p_x\ 2p_y|$$



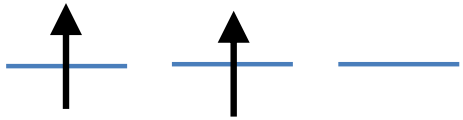
POLIELECTRONIC ATOMS

Exploiting the previous Slater determinants, we get

$$\psi_a(1,2) = \frac{1}{\sqrt{2}} 2p_x(1)\ 2p_x(2)\ [\alpha(1)\ \beta(2) - \alpha(2)\ \beta(1)]$$



$$\psi_b(1,2) = \frac{1}{\sqrt{2}} \left[2p_x(1)\ 2p_y(2)\ \alpha(1)\ \beta(2) - 2p_x(2)\ 2p_y(1)\ \alpha(2)\ \beta(1)\right]$$



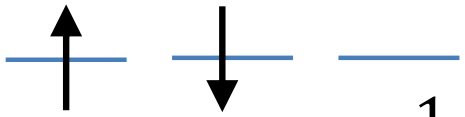
$$\psi_c(1,2) = \frac{1}{\sqrt{2}} \left[2p_x(1)\ 2p_y(2) - 2p_x(2)\ 2p_y(1)\right] \alpha(1)\ \alpha(2)$$

POLIELECTRONIC ATOMS

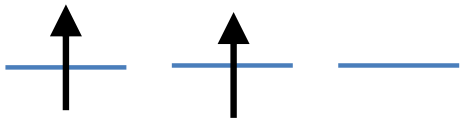
Now we ask: what it the probability of finding the 2 electrons in the same point of the space? In other words: what is the probability of finding the 2 electrons with the same spatial coordinates? Namely, $r_1 = r_2$ $\theta_1 = \theta_2$ $\phi_1 = \phi_2$

Dots indicate that the values of the spherical polar coordinates are equal

$$\psi_a(1,2) = \frac{1}{\sqrt{2}} 2p_x(\cdot)\, 2p_x(\cdot)\, [\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]$$



$$\psi_b(1,2) = \frac{1}{\sqrt{2}} 2p_x(\cdot)\, 2p_y(\cdot)[\,\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]$$



$$\psi_c(1,2) = 0$$

When the spins are parallel the probability is 0 (the square function is 0)

POLIELECTRONIC ATOMS

Being the wave functions continuous (for their «well-behavior»), the probability is almost zero also for coordinates of 1 and 2 close to each other, namely

$$\psi_c(1,2) \simeq 0 \qquad \text{for} \qquad r_1 \simeq r_2 \qquad \theta_1 \simeq \theta_2 \qquad \phi_1 \simeq \phi_2$$

As the 2 electrons are far apart, the interelectronic repulsion between them is smaller and ultimately the energy lower

Hund principle

When displacing electrons in degenerate orbitals, the electronic spin configurations with lower energy are those for which the spins are parallel

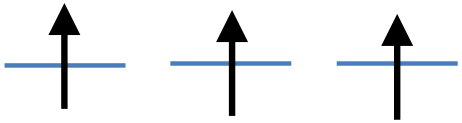
POLIELECTRONIC ATOMS

$$\psi_{\mathrm{C}}(\cdot) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\ 2p_y|$$

C

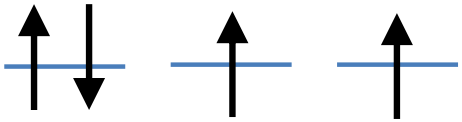
$$\psi_{\mathrm{N}}(\cdot) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\ 2p_y\ 2p_z|$$

N



$$\psi_{\mathrm{O}}(\cdot) = |1s\ \overline{1s}\ \ 2s\ \overline{2s}\ 2p_x\overline{2p_x}\ 2p_y\ 2p_z|$$

O



POLIELECTRONIC ATOMS

Excited states: to build excited states it is sufficient to promote electrons to higher energy spin-orbitals

$$\psi'_{\mathrm{He}}(\cdot) = |1s\ 2s|$$

$$\psi'_{\mathrm{He}}(\cdot) = |1s\ \overline{2s}|$$

$$\psi'_{\mathrm{He}}(\cdot) = |\overline{1s}\ \ \overline{2s}|$$

Three excited states can be built for He, differing in the spin configuration (triplet spin state)

$$\psi_{\mathrm{He}}(\cdot) = |\overline{1s}\ \ 1s|$$

For the **ground state** only one spin configuration is possible (singlet spin state)