Trolley's on Friday nights in Boston's Park Street Station can be quite crowded. Worse, often few people exit, making it quite hard for new riders to get on. There is one occasional exception: Homeless men not having bathed for months rarely have trouble. The crowd on the car miraculously parts, allowing such people spacious access no matter how crowded the car may have seemed. Electrons with parallel spins are like that. The parted crowd of other electrons is known as a Fermi hole.

The extension of the quantum description of one-electron atoms to atoms containing more than one electron is complicated by two unrelated things.

First, once there is more than a single electron, the combined effect of the electrical shielding of the nuclear charge and interelectron electrical repulsion jumbles things up. It turns out that these effects of nuclear shielding and electron-electron repulsion can be taken into account to a good approximation as relatively simple corrections to what we would expect if each electron were in the atom all by itself. This is known as the orbital approximation.

Second, and far more important, is that an amazing new property of the physical world comes into play, tracing to the fact that all electrons are, as far as we know, indistinguishable from one another. Once this indistinguishability is taken into account, through what is known as the Pauli exclusion principle, the result is a profound restriction on the way electrons can arrange themselves in an atom. It is this restriction that accounts for the periodic properties of the elements and so, ultimately, the structure of the physical world as we know it.

You may have learned the "rule" that no more than two electrons can be in the same orbital. If you have, you may also have puzzled about why such a rule is so. If you have decided, like many people who have been presented with just the rule without any explanation, that it has to do with electrical repulsion—that it reflects the electrons repelling one another due to their electrical charge—then you are in for a neat surprise. The "rule" instead traces to a deep algebraic property of nature that has nothing whatsoever to do with the charge on electrons! Perhaps you, like me, will find it fascinating that such a crucial aspect of the world has such a subtle origin.

The orbital approximation

In one-electron atoms, all of the energy levels for a given $n$ have the same energy. For example, in He+, the electron energy depends on the principle quantum number $n$. For example, the levels 3s, 3p and 3d all have the same energy

$$-E_e \frac{Z^2}{n^2} = -E_e \frac{4}{9}$$

Once more than one electron is present, we have to take into account the so-called shielding property of charges enclosed in a volume and the repulsion of the electrons for one another.
**Electrical shielding**

We have seen that for a given principle quantum number, \( n \), the smaller the orbital momentum quantum number, \( \ell \), the greater the electron probability amplitude close to the nucleus. This means that the smaller the orbital momentum of the electron, the greater will be the fraction of the electron near the nucleus. The result will be that electrons in orbitals with the same \( n \) but larger \( \ell \) will experience a reduced nuclear charge, due to cancellation (so-called shielding) of nuclear charge by the enhanced amount of electronic charge close to the nucleus from electrons with lower \( \ell \). The reduced nuclear charge means that electrons with higher orbital momentum are then held slightly less tightly. The hierarchy of relative energies therefor changes from

\[
1s < 2s, 2p < 3s, 3p, 3d < \ldots
\]

to

\[
1s < 2s < 2p < 3s < 3p < 3d < \ldots
\]

The net effect if that the different amount of penetration near the nucleus according to the orbital momentum results in the one-electron orbital energy depending on both the principle quantum number \( n \) and the orbital momentum quantum number \( \ell \).

Here are the details.

**Penetration and shielding**

We would like to understand the relative stability of many-electron subshells (fixed \( n \) but different \( \ell \)) in terms of the distribution of electron density for the different subshells. Here are the electron densities for the \( n = 3 \) electrons in a hydrogen atom.

\[|P_{3s}|^2\]

Hydrogen atom 3s (three peaks), 3p (two peaks) and 3d one peak) shell densities. Distance is in units of the Bohr radius, \( a_0 \). The vertical lines are the classical turning points (green for 3d, blue for 3p and black for 3s; the inner turning point for 3s is at \( r = 0 \)), and so bracket the classically allowed region for each shell density.

The vertical lines mark the allowed region of each subshell. Since the allowed region for the 3d is bracketed by that for the 3p, which in turn is bracketed by that for the 3s, we expect the average distance of the 3d electron to be closest to the nucleus, followed by the average distance of the 3p electron, and the 3s electron to farthest from the nucleus. The actual average distances, computed as

\[
\langle r_{3\ell} \rangle = \int_0^{\infty} \left| P_{3\ell}(r) \right|^2 r \, dr,
\]
are

\[
\begin{align*}
3s &= 13.5 \\
3p &= 12.5 \\
3d &= 10.5
\end{align*}
\]

Average distance, in \(a_0 = 0.527 \ \AA\), from the nucleus of hydrogen \(n = 3\) electrons.

This ordering of average distances may seem surprising, since we know in many-electron atoms, the 3s subshell is more stable than the 3p subshell, which is more stable than the 3d subshell, and this in turn might lead us to believe that in many electron atoms the 3s electron would be closest to the nucleus.

In fact, the origin of the greater stability of the 3s is due not to the average distance of the electron but instead to the relative amount of the electron density close to the nucleus in the different subshells. Here is a plot of the hydrogen 3s, 3p and 3d shell densities near the nucleus,

![Graph of hydrogen 3s, 3p, and 3d shell densities](image)

Hydrogen atom 3s (peak), 3p (quadratic rise from \(r = 0\)) and 3d (cubic rise from zero) shell densities near the nucleus. Distance is in units of the Bohr radius, \(a_0\).

and here is the fraction of electron density in each subshell within 1 \(a_0\) of the nucleus.

\[
\begin{align*}
3s &= 0.0099 \\
3p &= 0.0013 \\
3d &= 6.5 \times 10^{-6}
\end{align*}
\]

Fraction of hydrogen \(n = 3\) electron density within 1 \(a_0\) of the nucleus.

The results show that within 1 \(a_0\) of the nucleus the 3p shell density is only 13% of the 3s shell density, and the 3d shell density is essentially zero.

This means that both 3s and 3p electrons are present, a 3p electron will see less nuclear charge than a 3s electron, due to the shielding of the nucleus by the fraction of the 3s electron that is closer to the nucleus that the 3p electron. Similarly, a 3d electron will be shielded by both 3s and 3p electrons and so will see still less nuclear charge than a 3p electron. Since a 3d electron is shielded most, it will see the least nuclear charge and so be the least tightly bound. In this way we can understand why in many-electron atoms that within a shell, subshells fill in the order s, p, d, ….

Here is the fraction of electron density all of the subshells through \(n = 4\) within 1 \(a_0\) of the nucleus.
Fraction of hydrogen electron density within 1 $\alpha_0$ of the nucleus for the $n = 1, 2, 3,$ and 4 subshells.

See if you use these fractional electron densities to understand the filling order $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p$.

### Electrical repulsion

We can take account of the electrical repulsion of the electrons by a two step process. First, we assume each electron is described by an one-electron orbital, with energy modified by orbital momentum dependent shielding. Then, we use Coulomb’s law to evaluate the additional energy contribution due to the repulsion of the electron distributions.

### Two electrons

For example, He has two electrons. If we assume each electron is in a 1s orbital, then, ignoring interelectron repulsion, each electron contributes energy

$$-E_r \frac{Z^2}{n^2} = -E_r \frac{4}{1} = -4 E_r$$

for a total of $-8 E_r$. When the mutual repulsion of the two 1s charge distributions is taken into account, as described in the following subsection, there is an additional contribution of about $+5/2 E_r$. The combined effect of the attractions of each electron to the nucleus and the repulsion of the two electrons for one another is then

$$2 (-4 E_r) + 5 / 2 E_r = -11 / 2 E_r$$

To get a feeling for how this value compares with the actual value, we can use it to predict the first ionization energy of He. The energy balance in the ionization reaction

$$\text{He}(1 \text{s}^2) + \text{IE}_1 \rightarrow \text{He}^+ (1 \text{s}) + \text{e}^-$$

is

$$E(\text{He} 1 \text{s}^2) + \text{IE}_1 \rightarrow E(\text{He}^+ 1 \text{s})$$

since by definition of ionization energy, the ejected electron has zero kinetic energy. The predicted ionization energy is

$$\text{IE}_1 = E(\text{He}^+ 1 \text{s}) - E(\text{He} 1 \text{s}^2) = -4 E_r - (-11 / 2 E_r) = +3 / 2 E_r = 20.4 \text{ eV}.$$
Compare the percentage error in the zero order and first order approximations to the ionization energy of He.

To summarize, the idea of the orbital approximation is estimate the energy of a many-electron atom as the energies of the corresponding one-electron orbitals, taking into account electrical shielding, plus an additional amount due to electron-electron repulsion.

**Evaluation of the 1s1s one-electron-orbital repulsion**

The details of how to evaluate electrical repulsion between one-electron orbitals are described here, for the example of He 1s1s repulsion. The method works for any two one-electron orbitals, but it is easiest to use for repulsions between s orbitals.

The first order approximation to the ground state of helium atom in the one-electron-orbital approximation as to the zero order energy the expectation value of the repulsion $\frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$ of the two 1s electron charge distributions,

$$\left\langle \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \right\rangle = \frac{1}{4\pi\epsilon_0} \int \int \frac{\rho_{1s}(\mathbf{r})\rho_{1s}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r'},$$

where

$$\rho_{1s}(\mathbf{r}) = -e|\psi_{1s}(\mathbf{r})|^2 = -\frac{e}{4\pi r^2} P_{1s}(r)^2$$

is the charge density corresponding to the helium II ion 1s orbital. We can simplify the expectation value by transforming to rydberg units of energy and bohr units of length,

$$\left\langle \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \right\rangle = 2 E_r \int \int \frac{\rho_{1s}(\mathbf{r})\rho_{1s}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r'},$$

To proceed further we need to express $1/|\mathbf{r} - \mathbf{r}'|$ in terms the spherical polar coordinates of each electron. The expression is

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell + 1} \frac{r_<}{r_>^{\ell+1}} Y_{\ell m}(\theta' \phi')^* Y_{\ell m}(\theta \phi),$$

where $r_<$ and $r_>$ denote the lesser and greater of the two radial coordinates, respectively. Since the 1s charge densities are spherically symmetric, when this expression is substituted into the expectation value, the angular part of the integrations will be the two factors

$$\frac{1}{4\pi} \int Y_{\ell m}(\theta \phi) \sin(\theta) \, d\theta \, d\phi = \frac{1}{\sqrt{4\pi}} \int Y_{00}(\theta \phi)^* Y_{\ell m}(\theta \phi) \sin(\theta) \, d\theta \, d\phi = \sqrt{4\pi} \delta_{\ell 0} \delta_{m 0},$$

and

$$\frac{1}{4\pi} \int Y_{\ell m}(\theta' \phi')^* \sin(\theta') \, d\theta' \, d\phi' = \frac{1}{\sqrt{4\pi}} \int Y_{\ell m}(\theta \phi)^* Y_{00}(\theta \phi) \sin(\theta) \, d\theta \, d\phi = \sqrt{4\pi} \delta_{\ell' 0} \delta_{m' 0}. $$
In these expressions we have used the relations \( |Y_{00}|^2 = 1/(4 \pi) \) and \( Y_{00} = 1/\sqrt{4 \pi} \). Each of these factors evaluates to zero except for \( \ell = m = 0 \) and \( \ell' = m' = 0 \), in which they are equal to \( 1/\sqrt{4 \pi} \). Using these results, the expression for the expectation value of the 1s1s repulsion becomes

\[
\left( e^2 / \sqrt{4 \pi \varepsilon_0 | \mathbf{r} - \mathbf{r}' |} \right)
\]

\[
= 2 E_r \int \int \frac{\rho_{1s}(\mathbf{r}) \rho_{1s}(\mathbf{r}')}{| \mathbf{r} - \mathbf{r}' |} \, d\mathbf{r} \, d\mathbf{r}'
\]

\[
= 2 E_r \int_0^\infty \int_0^\infty \rho_{1s}(r)^2 \frac{1}{r} \rho_{1s}(r')^2 \, dr \, dr'
\]

\[
= 2 E_r \int_0^\infty \frac{1}{r} \rho_{1s}(r')^2 \left( \int_0^\infty \rho_{1s}(r)^2 \, dr \right) \, dr'
\]

\[
+ \int_0^\infty \rho_{1s}(r)^2 \left( \int_0^\infty \rho_{1s}(r')^2 \, dr' \right) \, dr
\]

\[
= 4 E_r \int_0^\infty \frac{1}{r} \rho_{1s}(r')^2 \left( \int_0^\infty \rho_{1s}(r)^2 \, dr \right) \, dr'
\]

This final expression is an example of Gauss' law, that a charge outside another charge distribution experience the charge distribution as a point charge at the center of the distribution. The final expression evaluates to \( 5 E_r / 2 \).

### Three electrons

Let's see what we get if we apply the orbital approximation to Li. We now have three electrons. What one-electron orbitals should we use for the electrons? Well, since we presumably want the ground state energy, I would propose that we use the lowest energy atomic orbitals. That is, let's assign each electron to a 1s orbital. Each electron would then contribute energy

\[
- \hbar c \, \text{Ry} \frac{Z^2}{n^2} = - \hbar c \, \text{Ry} \frac{9}{1} = -9 \hbar c \, \text{Ry}
\]

The electron-electron repulsion would be larger than in He, since the 1s charge distribution is more compact in Li; let's estimate the repulsion contribution to be twice as great, say \( +4 \hbar c \, \text{Ry} \). Also, now there would be two such contributions, since there are two different pairs of electrons repelling one another. In this way, we predict the total energy of Li to be

\[
3 (-9 \hbar c \, \text{Ry}) + 2 (4 \hbar c \, \text{Ry}) = -19 \hbar c \, \text{Ry}
\]

We could proceed in this way for all of the atoms in the periodic table. The approach is systematic and straightforward.

The problem is, however, that it cannot be correct! The reason is that this approach fails to predict the observed periodic variation in the properties of the atoms that is the basis of the periodic table. It predicts instead that the properties of atoms should vary in a continuous, non-periodic way, as more and more electrons are added as 1s orbitals.
The Pauli principle

That failure of our approach based on the orbital approximation tells us that there is something more to the structure of many-electron atoms than the effects of electron shielding and electron-electron repulsion. What could it be?

We had to decide how to assign electrons to one-electron orbitals. Since we want to determine the lowest energy state, we assigned each electron to the lowest energy, 1s orbital. This is the source of the problem. While it makes sense to put each electron in the lowest energy orbital, extraordinarily, this turns out not to be possible! What is observed instead is this:

A maximum of two electrons can occupy an orbital with the same \( n \), \( \ell \) and \( m \).

Here is what is going on.

Electron intrinsic magnetic moment

The story begins with the following fact about electrons. All electrons have an intrinsic magnetic moment—they behave like a bar magnet. One way to produce a magnetic moment is to create an electrical current in a loop of wire. Since electrons have a charge, when their magnetic moment was discovered it was thought that it was due to the electron spinning on its own axis, since this would produce a current. It was subsequently understood that the electron is not actually spinning, that its magnetic moment is an intrinsic property of the electron. Nonetheless, the magnetic moment is commonly referred to as the spin of the electron.

You may have played with bar magnets, and noticed that when they are parallel to one another (north pole next to north pole, south pole next to south pole), they repel each other, but when they are oppositely directed (anti-parallel), they attract each other. Other relative orientations produce corresponding repulsion or attraction intermediate in strength. Electrons behave similarly, but with an extraordinary difference.

Electron magnetic moments can only have two relative orientations.

This restriction to only two relative orientations is called space quantization, since the orientation of the spin can only take distinct values relative to an external axis (or to another spin). We have already seen that an electron with orbital momentum \( \ell \) can take \( 2\ell + 1 \) different orientations with respect to an external axis (or to another angular momentum), corresponding to the \( 2\ell + 1 \) different values of the quantum number \( m \). Since the electron magnetic moment can only take \( 2s + 1 = 2 \) orientations, we can interpret this to mean that the electron has a spin momentum quantum number \( s \) equal to 1/2, and the two possible orientations correspond to the two possible projection quantum numbers \( m_s = +1/2 \) and \( m_s = -1/2 \). The two orientations of the electron spin are sometimes referred to as "up" and "down" and conventionally represented by arrows, \( \uparrow \) and \( \downarrow \), respectively. All that is important is that the spin magnetic moments may either be parallel or antiparallel, that no other relative orientations are possible.

Indistinguishability of electrons

Now, what does electron spin have to do with putting electrons into orbitals? The answer starts with the observation that electrons are all identical (as far as we know). In order to account for this, we have to be sure that no electrons are treated preferentially. In particular, this means that when we label electrons in wavefunctions, we have to make sure that we do so in such a way that all physical properties we calculate do not depend on which electron we call 1, which we call 2, and so on. This non-preferential labelling is called symmetrization.
One way to ensure that numbering of electrons doesn't matter is to arrange things so that if we renumber electrons, then the wavefunction does not change. This requirement is actually too rigid. If we allow that the sign of the wavefunction might change, that would still be OK, since it is the square of the wavefunction that determines electron density, and when we square the wavefunction, any sign change disappears.

So, there are two ways to symmetrize many-electron wavefunctions. Many-electron wavefunctions that have been adjusted so that the sign of the wavefunction does not change on relabelling any two electrons are said to be symmetric. Many-electron wavefunctions that have been adjusted so that the sign of the wavefunction does change on relabelling any two electrons are said to be antisymmetric.

Be careful to distinguish the meaning of the terms symmetrization, symmetric, and antisymmetric.

In considering the symmetry of many-electron wavefunctions with respect to exchange of electron labels, we have to consider both the spatial and spin parts of the wavefunction. In the examples below we will see just what this means, but one procedure is to write the wavefunction as a product of space and spin parts, and to consider the symmetry of each part separately.

With this background, we can state one of the most profound aspects of quantum mechanics for the material world. It is known as the Pauli principle:

The overall wavefunction—spatial and spin parts—must change sign if any two electrons are relabeled.

That is, many-electron wavefunctions must be antisymmetric.

More generally, the wave function of any quantum system composed of entities with half-odd intrinsic angular momentum (spin quantum number 1/2, 3/2, 5/2, …) must be antisymmetric. The wave function of any quantum system composed of entities with integer intrinsic angular momentum (spin quantum number 0, 1, 2, …) must be symmetric. An example is photons, the packets of light energy. Photons have intrinsic spin 1, and so the wavefunction of a collection of photons must be symmetric with respect to the relabelling of any two photons.

Electronic configurations in atoms

The Pauli principle requires that the total electronic wavefunction is antisymmetric with respect to exchange on labels on any two electrons. Let's see what consequences this has as we add electrons to one-electron orbitals.

The configuration of an atom consists of

- the set of orbitals (specified by \( n \), \( \ell \), and \( m \)) occupied by electrons, and
- the number of electrons in each orbital.

The ground-state configuration has all of the electrons in the lowest energy orbitals possible.

Hydrogen

For hydrogen the ground-state configuration is

\[ H 1s \]

Since there is only one electron, the Pauli principle doesn't apply.
## Helium

For helium, we can write

He $1s^2$

Now, because we more than one electron, we have to take the Pauli principle into account; the overall wavefunction must be antisymmetric. To see the symmetry of the wavefunction, we need to write it in terms of the space and spin parts of each electron's wavefunction. For example, if we have both electrons with spin up, then the wavefunction would be

$$1s(1)1s(2) \times \uparrow(1)\uparrow(2)$$

Exchanging the electron labels this becomes

$$1s(2)1s(1) \times \uparrow(2)\uparrow(1)$$

This is just the same as the original function, except that the parts are written in different order. This means that this function is symmetric and so does not satisfy the Pauli principle. The same thing would be true if both electrons had spin down,

$$1s(1)1s(2) \times \downarrow(1)\downarrow(2)$$

If we want both electrons to be in 1s spatial orbitals, then the spatial part of these wavefunction is necessarily symmetric. This means that to satisfy the Pauli principle we need to make the spin part antisymmetric. If we choose one spin up and one spin down, say

$$\uparrow(1)\downarrow(2)$$

then on exchanging labels we get

$$\uparrow(2)\downarrow(1)$$

This is neither the same nor the negative of the starting function. This means that this spin part does not have any exchange symmetry. This is actually progress, however, for we can convert the function into one that does have exchange symmetry by combining the original spin part of the wavefunction and its exchanged form, as

$$\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)$$

or

$$\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)$$

On exchange, the first form becomes

$$\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2) \xrightarrow{1 \leftrightarrow 2}$$

$$\uparrow(2)\downarrow(1) + \downarrow(1)\uparrow(2) = +[\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)]$$

and so is symmetric. The second form becomes

$$\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2) \xrightarrow{1 \leftrightarrow 2}$$

$$\uparrow(2)\downarrow(1) - \downarrow(1)\uparrow(2) = -[\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)]$$

and so is antisymmetric. Since we want the spin part to be antisymmetric, we use the second form and so write the configuration of He as

$$1s(1)1s(2) \times [\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)]$$
## Lithium

For lithium we can try, as we did before,

\[
\text{Li } 1s^3
\]

This means the spatial part of the wavefunction would be

\[
1s(1)1s(2)1s(3)
\]

which is symmetric. This in turn means that, to satisfy the Pauli principle, the spin part would again have to be antisymmetric. Since there are only two possibilities for each spin, up or down, the third spin must be the same as one of the other two, and so the spin part would be symmetric with respect to exchange of those two spin. Therefore, we come to the key consequence of the Pauli principle for many-electron atoms:

If more than two electrons are in the same orbital \((n, \ell, \text{ and } m\) the same), the spin function cannot be made antisymmetric and so the overall wavefunction cannot satisfy the Pauli principle.

If we try instead to construct an antisymmetric spatial orbital, the spatial part of the wavefunction will always vanish!

The only solution is to add the third electron to a different spatial orbital. From the analysis of the effects of shielding, the next lowest energy orbital is the 2s orbital, and so we try instead the configuration

\[
\text{Li } 1s^22s
\]

If we do this, we can make the overall wavefunction—spatial and spin parts—antisymmetric. It was easy to write down the antisymmetric wavefunction for two electrons, in helium. For more than two electrons there are techniques to make the process more systematic. We don't need to learn these now, but here is the result for \text{Li } 1s^22s, assuming the electron in the 2s orbital has spin up.

\[
\text{Li } 1s^22s =
\begin{align*}
+ & 1s\uparrow(1) \times [1s\downarrow(2)2s\uparrow(3) - 2s\uparrow(2)1s\downarrow(3)] \\
- & 1s\downarrow(1) \times [1s\uparrow(2)2s\uparrow(3) - 2s\uparrow(2)1s\uparrow(3)] \\
+ & 2s\uparrow(1) \times [1s\uparrow(2)1s\downarrow(3) - 1s\downarrow(2)1s\uparrow(3)]
\end{align*}
\]

The notation \(1s\uparrow(1)\) means electron 1 is in a 1s orbital with spin up, that is, \(1s(1)\uparrow(1)\), etc. It is easy to see that each term in the square brackets is antisymmetric in exchange of labels 2 and 3. For example,

\[
1s\downarrow(2)2s\uparrow(3) - 2s\uparrow(2)1s\downarrow(3) \xrightarrow{2s^3} 1s\downarrow(3)2s\uparrow(2) - 2s\uparrow(3)1s\downarrow(2) = -[1s\downarrow(2)2s\uparrow(3) - 2s\uparrow(2)1s\downarrow(3)]
\]

It is only a little harder to show that this wavefunction is also antisymmetric in exchange of labels 1 and 2, and of labels 1 and 3. See if you can do this as a study problem.
Pauli exclusion principle

We can summarize all of this by saying that no more than two electrons can be in the same orbital, and then their spins must be oppositely directed. This is usually expressed as the Pauli exclusion principle:

No two electrons can have the same set of four quantum numbers \( n, \ell, m, \text{ and } m_s \).

It is helpful to understand that the Pauli exclusion principle is thus a special case of the Pauli principle when applied to many-electron atoms. Systematic application of the Pauli principle to the atoms of each of the elements is the key to why atoms show the periodic properties that they do.

Relative stability of 1s2p configurations—Fermi holes and Fermi heaps

A striking example of the consequences of the Pauli principle is the lowest excited configuration of He that is produced by absorption of light energy. The oscillating electric field of the light distorts the excited electron from its original spherical shape (as 1s) to a two-lobed shape (as 2p) and so the resulting electronic configuration is

\[
\text{He 1s2p}
\]

The question arises, what is the relative orientation of the spins of the two electrons? It turns out that the arrangement with both spins in the same direction, say

\[
1s(1)2p(2) \times \uparrow(1)\uparrow(2),
\]

is much more stable (lower in energy) than the arrangement with the spins oppositely directed, say

\[
1s(1)2p(2) \times \uparrow(1)\downarrow(2).
\]

This is a very surprising result if we think just in terms of the interaction energy of bar magnets. That is, we would expect the arrangement \( \uparrow(1)\uparrow(2) \), in which the magnetic poles are north to north, would be less stable than the arrangement \( \uparrow(1)\downarrow(2) \), in which the magnetic poles are north to south. In fact, it was just this surprising behavior that led Pauli to his principle in the first place.

The origin of the surprising stability of the \( \uparrow(1)\uparrow(2) \) arrangement is that thereby the two electrons stay out of each other's way, forming what is called a Fermi hole, and so their electrical repulsion is reduced. Just the opposite happens when the spins are arranged as \( \uparrow(1)\downarrow(2) \): When the spins are oppositely directed, the electrons actually clump together, forming what is called a Fermi heap, with the result that the electrical repulsion between the electrons is enhanced.

Fermi holes and Fermi heaps are consequences of the symmetry with respect to relabelling of pairs of electrons—the exchange symmetry—of the spatial part of the many-electron wavefunction. To see this, let's construct the symmetrized wavefunctions corresponding to the alternative arrangements of the spins.

If the spins are parallel, then the spin part of the wavefunction is symmetric. This means that, for the overall wavefunction will be antisymmetric, the spatial part must be antisymmetric.

\[
\psi_{\uparrow\uparrow} = [1s(1)2p(2) - 1s(2)2p(1)] \times \uparrow(1)\uparrow(2).
\]

If instead the spin are antiparallel, then the spin part of the wavefunction is antisymmetric. This means that the spatial part must be symmetric so that the overall wavefunction will be antisymmetric.

\[
\psi_{\uparrow\downarrow} = [1s(1)2p(2) + 1s(2)2p(1)] \times [\uparrow(1)\downarrow(2) - \uparrow(2)\downarrow(1)].
\]
Now, let's look carefully at the spatial parts of these alternative wavefunctions. For $\psi_{1\uparrow}$, the spatial part vanishes when the coordinates of the two electrons are the same, that is, when the two electrons are in the same place, say $x, y, z$. The reason is that then the numerical value of the spatial functions $1s(1)$ and $1s(2)$ will be the same and the numerical value of the spatial functions $2p(1)$ and $2p(2)$ will be the same. The result is that the two terms in the spatial part of the wavefunction will exactly cancel.

$$1s(x_1, y_1, z_1)2p(x_2, y_2, z_2) - 1s(x_2, y_2, z_2)2p(x_1, y_1, z_1)$$

This means that there is zero probability of the two electrons being in the same place in physical space. The Pauli principle causes electrons with parallel spins to stay out of one another's way. It is as if each electron is surrounded by an exclusion zone into which the other electron may not penetrate. The result is a correspondingly decreased electron-electron repulsion, and so a more stable arrangement that would be the case had we not taken the Pauli principle into account.

One the other hand, for $\psi_{\uparrow\downarrow}$, the spatial part doubles when the two electrons are in the same place. The reason is now there is two terms in the spatial part of the wavefunction add rather than subtract.

$$1s(x_1, y_1, z_1)2p(x_2, y_2, z_2) + 1s(x_2, y_2, z_2)2p(x_1, y_1, z_1)$$

This means that the probability of the two electrons being in the same place in physical space is double what it would be if we did not take the Pauli principle into account. Said differently, the Pauli principle causes electrons with antiparallel spins to clump together, forming a heap of electrical charge. This clumping results in a correspondingly increased electron-electron repulsion, and so a less stable arrangement that would be the case had the electron spins been parallel.

It is important to understand that the Fermi hole and Fermi clump do not come about because of electron-electron repulsion. Rather, they come about because of the algebraic consequences of the exchange symmetry of the spatial part of the many-electron wavefunction. The subsequent energetic consequences do arise because of the changes in electron-electron repulsion, of course, but Fermi holes and Fermi heaps would arise independently of the electron charge.

## Visualization of 1s2p Fermi holes and Fermi heaps

Here is a way to visualize the He 1s2p Fermi hole and Fermi heap. We can construct the spatial part of the wavefunctions, and then look at how the probability density of one electron varies about the location of the other electron.

Let's assume that the electric field of the light is polarized along the $y$ direction. This means that the electron will be excited from the 1s orbital to a $2p_y$ orbital. We will need, therefor, He one-electron wavefunctions for 1s and 2p$_y$. The radial parts of these wavefunctions are

$$n \ell \rho$$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$2 e^{-\rho}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\frac{e^{-\rho/\sqrt{2}}}{\sqrt{\pi}}$</td>
</tr>
</tbody>
</table>

The angular parts of the wavefunction are

<table>
<thead>
<tr>
<th>label</th>
<th>function</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$</td>
<td>$\frac{1}{\sqrt{\pi}}$</td>
</tr>
<tr>
<td>$p_y$</td>
<td>$\frac{1}{\sqrt{\pi}} \sin[\theta] \sin[\phi]$</td>
</tr>
</tbody>
</table>
The full 1s and 2p\textsubscript{y} wavefunctions are therefore

\begin{align*}
\text{label} & \quad \text{full wavefunction} \\
1s & \quad \frac{e^{-\rho}}{\sqrt{\pi}} \\
2p_y & \quad \frac{e^{-\rho/2} \rho^2 \sin[\theta] \sin[\phi]}{4\sqrt{2}\pi}
\end{align*}

Here is how the visualization looks, for one electron at \( y = -2a_0 \) in the \( xy \) plane.

![Visualization of 2p\textsubscript{y} orbital](http://quantum.bu.edu/notes/QuantumMechanics/FermiHolesAndHeaps/FermiHeapHole1s2py.gif)

He 1s2p\textsubscript{y} Fermi heap (left) and Fermi hole (right). The post marks the position of one electron, at \( y = -2a_0 \) in the \( xy \) plane. The height of the surface is the probability density of the other electron. The Fermi heap shows the clumping of the two electrons, while the Fermi hole shows that the two electrons are never found in the same place.

An animation of the visualization, showing the variation of the probability density for locations of one electron on a ring of radius 2 \( a_0 \) in the \( xy \) plane, is available at

http://quantum.bu.edu/notes/QuantumMechanics/FermiHolesAndHeaps/FermiHeapHole1s2py.gif

The figure above is taken from this animation. The directional character of the 2p\textsubscript{y} orbital accounts for the coming and going of the Fermi heap in the animation.

## Relative stability of 2p\textsuperscript{2} configurations

When \( \ell \) is greater than zero, more than two electrons can be accommodated in a subshell. The question arises as to the relative spin directions of electrons in different orbitals, that is, with different \( m \) values. The answer is that the lowest energy arrangement is when the spins are in the same direction. This is another consequence of the Pauli principle, as we will see now.

### Configurations

If we ignore for the moment the requirement of the Pauli principle, namely that the combined wavefunction (spatial and spin) of the two electrons be antisymmetric with respect to exchange of the electrons, then there are five possible configurations.

\begin{align*}
\text{unsym}_1 & = 2p_x(1)\uparrow(1) \ 2p_x(2)\downarrow(2) \\
\text{unsym}_2 & = 2p_x(1)\uparrow(1) \ 2p_y(2)\uparrow(2) \\
\text{unsym}_3 & = 2p_x(1)\uparrow(1) \ 2p_y(2)\downarrow(2) \\
\text{unsym}_4 & = 2p_x(1)\downarrow(1) \ 2p_y(2)\uparrow(2)
\end{align*}
unsym₃ = \( 2p_x(1) \uparrow (1) 2p_y(2) \downarrow (2) \)

We'll refer to these configurations by their numbers. Configuration unsym₁ has both electrons in the same \((2p_x)\) orbital. The other four configurations have the electrons in different orbitals \((2p_x\) and \(2p_y)\); any pair of \(2p\) orbitals would do as well).

None of these configurations is symmetrized, that is they are neither symmetric nor antisymmetric. For example, exchanging the electron labels in configuration unsym₁ gives

\[
2p_x(1) \uparrow (1) 2p_x(2) \downarrow (2) \xrightarrow{1 \leftrightarrow 2} 2p_x(2) \uparrow (2) 2p_x(1) \downarrow (1)
\]

but this is not equal to \(+\) or \(-\) times configuration unsym₁.

To satisfy the Pauli principle, these configurations must be symmetrized to be antisymmetric, that is, so that they give either themselves or themselves multiplied by \(-1\) when the two electron labels are exchanged.

A convenient way to symmetrize these configurations is to symmetrize their space and spin parts separately and then form products of symmetrized space and spin parts so that the overall wavefunctions are antisymmetric. Here are the results.

\[
sym₁ = 2p_x(1) 2p_y(2) \times [\uparrow (1) \downarrow (2) - \uparrow (2) \downarrow (1)]
\]

\[
sym₂ = [2p_x(1) 2p_y(2) + 2p_y(2) 2p_x(1)] \times [\uparrow (1) \downarrow (2) - \uparrow (2) \downarrow (1)]
\]

\[
sym₃ = [2p_x(1) 2p_y(2) - 2p_y(2) 2p_x(1)] \times \uparrow (1) \uparrow (2)
\]

\[
sym₄ = [2p_x(1) 2p_y(2) - 2p_y(2) 2p_x(1)] \times [\uparrow (1) \downarrow (2) + \uparrow (2) \downarrow (1)]
\]

\[
sym₅ = [2p_x(1) 2p_y(2) - 2p_y(2) 2p_x(1)] \times \downarrow (1) \downarrow (2)
\]

The spatial parts of symmetrized configurations sym₁ and sym₂ are symmetric, their spin parts are antisymmetric, and so the overall wavefunctions are antisymmetric. The spatial parts of symmetrized configurations sym₁, sym₃, and sym₄ are antisymmetric, their spin parts are symmetric, and so again the overall wavefunctions again are antisymmetric.

Symmetrized configurations sym₁ and sym₂ correspond to the spins pointing in opposite directions. The configuration sym₁ can be represented as

\[
\begin{array}{c}
\uparrow \\
\downarrow \\
2p_x \quad 2p_y \quad 2p_z
\end{array}
\]

that is, both electrons in the same orbital with opposite spins. The configuration sym₂ can be represented as

\[
\begin{array}{c}
\uparrow \\
\downarrow \\
2p_x \quad 2p_y \quad 2p_z
\end{array}
\]

that is, the electrons in different orbitals with opposite spins.

Symmetrized configurations sym₃, sym₄ and sym₅ correspond to both spins pointing in the same direction. A way to see this is first to realize that in this case the total spin is \(S = s_1 + s_2 = 1\); then, because spin is an angular momentum (like orbital momentum \(l\)) it can have three different value of \(m_S\), namely 1, 0 and \(-1\). Configuration sym₁ has \(m_S = 1\), configuration sym₄ has \(m_S = 0\), and configuration sym₅ has \(m_S = -1\). These three configurations all have the same energy and form what is called a spin triplet. They can be collectively represented as
that is, the electrons in different orbitals with the same spins.

**Relative energies**

There are two aspects to consider in deciding the relative stability of the three arrangements (both electrons in the same orbital with opposite spins, electrons in different orbitals with opposite spins, or electrons in different orbitals with the same spin), namely the magnetic interactions between the electrons, due to their spin, and the electrical repulsions between the electrons, due to their negative charge.

The spin of the electron is due to its intrinsic magnetic moment—the electron behaves magnetically as a bar magnet. Now, bar magnets attract one another when they are anti-parallel to one another (north pole adjacent to south pole), and repel one another when they are parallel (north poles adjacent). This means that magnetically, electrons with the same spin are the least stable.

The charges of the electrons repel one another according to Coulomb's law, so that the closer the electrons are, the more they repel. This means that electrically, electrons in the same orbital are the least stable, since they then occupy the same part of space.

So, we have two competing effects, which we can tabulate as

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Magnetic stability</th>
<th>Electrical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stable (north–south)</td>
<td>unstable (same region of space)</td>
</tr>
<tr>
<td>2p_x 2p_y 2p_z</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stable (north–south)</td>
<td>stable (spatially separated)</td>
</tr>
<tr>
<td>2p_x 2p_y 2p_z</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>unstable (north–north)</td>
<td>stable (spatially separated)</td>
</tr>
<tr>
<td>2p_x 2p_y 2p_z</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Because magnetic effects are generally much weaker than electrical effects, we can conclude that the arrangement with both electrons in the same orbital with opposite spins is the least stable of the three possible arrangements. The other two arrangements each have the electrons in different orbitals and so should have the same electrical interaction. Therefore we might expect that the most stable arrangement would be when the electrons have the opposite spins, since then they are attracted magnetically. What is observed is just the reverse; the arrangement with the electrons in different orbitals with the same spin is most stable.

**Fermi hole and Fermi heap**

Since this is just the opposite of what is predicted based on magnetic interactions, the cause must be electrical. So to see what is going on, we need to compare the space parts of the wavefunctions for the electrons in different orbitals, since only the spatial distribution of the electrons can affect their mutual electrical repulsion.

The space wavefunction when the two electrons have the same spin is

$$2p_x(1)2p_y(2) - 2p_x(2)2p_y(1)$$
This function has the remarkable property that it vanishes when both electrons are in the same place (that is, when their coordinates are the same, which corresponds to $1 = 2$). This means that the probability of the two electrons being in the same place is zero. We can say that when electrons have an antisymmetric space wavefunction, they stay away from one another. This effect is called a Fermi hole. As a consequence, the electrical repulsion between the two electrons is lessened.

Just the opposite effect occurs when the two electrons have anti-parallel spins. The space wavefunction in this case is

$$2p_x(1)2p_y(2) + 2p_x(2)2p_y(1)$$

This function becomes twice as large when both electrons are in the same place (when $1 = 2$). This means that the probability of the two electrons being in the same place is much greater than the probability of each electron being there separately. We can say that when electrons have a symmetric space wavefunction, they clump together. This effect is called a Fermi heap. As a consequence, the electrical repulsion between the two electrons is increased.

The Fermi heap also occurs in the arrangement when both electrons are in the same orbital, and there its destabilizing effect is even greater, since the electrons are in the same orbital and thus closer together.

Everything can be summarized as follows.

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Magnetic stability</th>
<th>Electrical stability</th>
<th>Net effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\uparrow\downarrow$</td>
<td>stable</td>
<td>very unstable</td>
<td>very unstable</td>
</tr>
<tr>
<td>$2p_x$ $2p_y$ $2p_z$</td>
<td>(north–south)</td>
<td>(same region and Fermi heap)</td>
<td></td>
</tr>
<tr>
<td>$\uparrow\downarrow$</td>
<td>stable</td>
<td>unstable</td>
<td>unstable</td>
</tr>
<tr>
<td>$2p_x$ $2p_y$ $2p_z$</td>
<td>(north–south)</td>
<td>(separated but Fermi heap)</td>
<td></td>
</tr>
<tr>
<td>$\uparrow\uparrow$</td>
<td>unstable</td>
<td>very stable</td>
<td>stable</td>
</tr>
<tr>
<td>$2p_x$ $2p_y$ $2p_z$</td>
<td>(north–north)</td>
<td>(separated and Fermi hole)</td>
<td></td>
</tr>
</tbody>
</table>

The conclusion from all of this analysis is, if possible, put electrons in different spatial orbitals, with spins in the same direction, since this arrangement has the lowest energy.

**Visualization of 2p2p Fermi holes and Fermi heaps**

Here is a way to visualize the C 2p2p Fermi hole and Fermi heap. We can construct the spatial part of the wavefunctions, and then look at how the probability density of one electron varies about the location of the other electron.

The radial part of the $2p_x$ and $2p_y$ these wavefunctions is

$$n \ell P_{n \ell} \frac{e^{\pm i \phi} \rho}{2 \sqrt{6}}$$

The angular parts of the wavefunction are

<table>
<thead>
<tr>
<th>label</th>
<th>function</th>
</tr>
</thead>
<tbody>
<tr>
<td>$px$</td>
<td>$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos(\phi) \sin(\theta)$</td>
</tr>
<tr>
<td>$py$</td>
<td>$\frac{1}{2} \sqrt{\frac{3}{\pi}} \sin(\theta) \sin(\phi)$</td>
</tr>
</tbody>
</table>

The full $2p_x$ and $2p_y$ wavefunctions are therefore
Here is how the visualization looks, for one electron at \( y = -2 a_0 \) in the \( xy \) plane.

An animation of the visualization, showing the variation of the probability density for locations of one electron on a ring of radius \( 4 a_0 \) in the \( xy \) plane, is available at

http://quantum.bu.edu/notes/QuantumMechanics/FermiHolesAndHeaps/FermiHeapHole2px2py.gif

The figure above is taken from this animation. The directional character of the 2p orbitals accounts for the coming and going of the Fermi heap in the animation.