

Periodic Table of Elements

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Figure 1: The periodic table, from www.ptable.com. There are other nice ones there, listing various other properties.

Part I: The elements

As we all know, all matter is made of atoms. The atoms themselves consist of a nucleus plus electrons. The nucleus is very small, on the scale of $10^{-15}m$, and contains protons and neutrons. Different elements are labelled by their **atomic number** Z , which is the number of protons in the nucleus. Of course, a neutral atom has Z electrons moving around the nucleus, in an electronic cloud whose typical size is of the order of $10^{-10}m = 1\text{\AA}$. An atom with fewer/more electrons than its Z is called an **ion**, and is electrically charged.

There are around 100 stable elements, with $Z = 1, 2, 3, \dots$. They have names such as hydrogen, H, for $Z = 1$; helium, He, for $Z = 2$, etc. They are grouped in the **periodic table** according to their properties. There are various ways to display this periodic table; one possible example is shown in Fig. 1. For each element, the top left number is the atomic number Z . These increase monotonically from left to right, and from top to bottom. The symbol of the element is also listed with the name written underneath. The number below is the **mass number**, i.e. the total number of protons plus neutrons in the nucleus (electrons are so much lighter than the nucleons, that their contribution to the atom's mass is negligible). The number of nucleons is an integer, of course, so you may be surprised to see a non-integer value listed in most cases. The explanation is that many elements come in several **isotopes**, each with a different number of neutrons. Some of these are stable, some are unstable to nuclear reactions.

For example, for potassium ^{39}K , the mass number is 39.0938. According to Wikipedia (not necessarily the most trustworthy source of information, but for something like this it will normally do), K has 25 known isotopes, of which 3 occur naturally. Of these, the most abundant is ^{39}K ,

which therefore has 20 neutrons, and abundance of about 93.3%. $^{19}_{41}\text{K}$ (22 neutrons) is also stable, but with abundance of 6.7%. Finally, $^{19}_{40}\text{K}$, with 21 neutrons, is unstable, but only occurs in 0.012% abundance. It can decay to either $^{18}_{40}\text{Ar}$, or to $^{20}_{40}\text{Ca}$ – you should be able to figure out how is that possible, but in any event this explains why bananas are radioactive. The other unstable isotopes do not occur naturally but can be created using cyclotrons (eg, TRIUMF has a program to create radioactive isotopes with fairly short lifetimes, for medicinal purposes). In any event, you can see why the mass number of K is just slightly over 39.

Finally, there are some numbers listed to the right, whose meaning we'll discuss in a bit. Before that, let me express my hope that you will spend a bit of time looking through the posted supplementary notes from N. Ingle, where he reviews nicely some of the history behind both establishing that atoms have this structure, and understanding how to order them in the periodic table. At the very least, I hope you know that proving that matter is made of atoms is actually a recent development, on the order of 100y old only! Of course, some of the ancient Greeks speculated that this is how things stand, but in modern physics we have to check any theory by experiments. Our microscopic understanding of the structure of matter has come very far, indeed, in a very short time!

The last step is to understand what are the electrons doing. For this, we need to solve Schrödinger's equation, to find what energy levels are available to them. We know that if we can ignore interactions between electrons, in the ground-state (the most stable state) the lowest available levels will be fully occupied according to Pauli's principle.

So let's ignore interactions, to begin with, and I'll tell you a bit later how we can account for them in an averaged fashion. Consider a nucleus with a given Z , meaning a positive charge of Ze , and a single electron – so we can find its spectrum. Because of the spherical symmetry of the problem, it is convenient to work with spherical coordinates r, θ, ϕ . Schrödinger's equation reads:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{kZe^2}{r} \right] \phi(r, \theta, \phi) = E\phi(r, \theta, \phi)$$

where I'll use the simpler notation $k = 1/(4\pi\epsilon_0)$. Even though this is a quite complicated equation, it can be solved exactly and has rather simple solutions. Let me first mention that it has eigenstates for all energies $E > 0$ – these are states where the electron has sufficiently large kinetic energy that it is not bound to the nucleus. Clearly, we're not interested in these states here.

There is no doubt that you will go through the math of this problem before completing a physics degree, so let me just list the results here, for the bound states with $E < 0$. Then, we'll discuss qualitatively what the wavefunctions look like.

It turns out that we need 4 quantum numbers to fully index all bound quantum states, 3 for the spatial part (three integers n, l, m) and one for the spin ($\sigma = \uparrow, \downarrow$):

- $n = 1, 2, \dots$ is known as the **principal number**. It controls the value of the energy:

$$E_n = -\frac{mc^2}{2} \frac{(Z\alpha)^2}{n^2} = -\frac{Z^2}{n^2} \cdot 13.6\text{eV}$$

where

$$\alpha = \frac{ke^2}{\hbar c} \approx \frac{1}{137}$$

is a dimensionless constant known as the **fine structure constant**. Traditionally, people also used to call levels with $n = 1, 2, \dots$ as K, L, M, ..., but I will probably not do that much.

- $l = 0, 1, \dots, n-1$ is called **the angular momentum**. It defines the size of the total angular of the electron – this value is actually $\hbar\sqrt{l(l+1)}$. Note that the maximum allowed value of l depends on n ! It is traditional to call states with $l = 0, 1, 2, 3, \dots$ as s, p, d, f, \dots and I will certainly do so.

To be more specific, if I say $1s$, it means $n = 1$ and $l = 0$; $3p$ means $n = 3$ and $l = 1$, etc. The integer tells you the value of n , and the letter gives the value of l .

- $m = -l, -l+1, \dots, l-1, l$ is another integer that can take $2l+1$ distinct values for a given value of l . This is the **projection of the angular momentum along an axis**, which is also quantized to the value $m\hbar$. This should remind you of what I said about the spin and its allowed values for its projection along an axis – the reason for the similarity is that the spin is an angular momentum so it has the same types of quantization rules.

- the spin $\sigma = \uparrow, \downarrow$, since the electrons are spin-1/2 fermions. So, going back to our example, there are 2 distinct quantum states for an $1s$ orbital. Because $l = 0 \rightarrow m = 0$, but we still have $\sigma = \uparrow, \downarrow$. Same is true for $2s, 3s, \dots$, they all have $l = 0, m = 0$ and $\sigma = \uparrow, \downarrow$.

For a $2p, 3p, \dots$ orbital, we have $l = 1$ therefore $m = -1, 0, 1$ and $\sigma = \uparrow, \downarrow$, so now we have 6 possible combinations, therefore 6 distinct states in a p orbital (3 values of m , each of which can have either spin). For a $3d, 4d, \dots$ orbital, we have $l = 2$, therefore $m = -2, -1, 0, 1, 2$, and $\sigma = \uparrow, \downarrow$, so 10 distinct states in a d orbital. Etc, etc. So these are the quantum numbers.

As already stated, the eigenenergies depend only on n , so the levels are highly degenerate. The degeneracy is 2 for $n = 1$ (only $1s$ levels possible); $2 + 6 = 8$ for $n = 2$ (both $2s$ and $2p$ levels possible), $2 + 6 + 10 = 18$ for $n = 3$ ($3s, 3p, 3d$ levels possible), etc.

The l and m help index all the different eigenfunctions corresponding to the same n . To see the wavefunctions, their full formulae and various ways to represent their spatial structure, I suggest you explore Orbitron at winter.group.shef.ac.uk/orbitron/ (if you find a better website, let me know). I will list the main points, which is what I want you to know. First, the spatial part of the wavefunction factorizes into a part that depends only on r , and one that depends only the angles:

$$\phi_{n,l,m}(r, \theta, \phi) = R_{nl} \left(\frac{2Z}{na_B} r \right) Y_{lm}(\theta, \phi)$$

Here

$$a_B = \frac{\hbar}{m c \alpha} \approx 0.5A$$

is known as the Bohr radius, and gives the typical size of the wavefunction. To be more precise, look at the dimensionless combination

$$\rho = \frac{2Z}{na_B} r$$

on which the radial part depends. For example, $R_{10}(\rho) \propto e^{-\rho/2}$ (I will not list the normalization constants); $R_{20}(\rho) \propto (2 - \rho)e^{-\rho/2}$, $R_{21}(\rho) \propto \rho e^{-\rho/2}$, etc. So these are very simple functions. They all have an exponential so they decrease fast enough to be normalizable, times some simple polynomial.

I sketched some of these radial functions in Fig. 2, to show their qualitative features. The important things to remember, regarding the shape of the radial parts, are:

(i) all s orbitals are finite at $\rho = 0$, whereas all p orbitals increase proportionally to ρ near the origin, all d orbitals go like ρ^2 near origin, f orbitals go like ρ^3 near origin, i.e. $R_{nl}(\rho) \sim \rho^l$ for $\rho \rightarrow 0$. They all decrease exponentially like $e^{-\rho/2}$ as $\rho \rightarrow \infty$.

(ii) somewhere in between 0 and ∞ , an ns orbital has $n - 1$ nodes (i.e., finite values of ρ where it vanishes); so: none for $1s$, 1 for $2s$, 2 for $3s$ etc. A np orbital has $n - 2$ nodes; so $2p$ (first allowed p orbital) has no nodes, $3p$ has one, $4p$ has two, etc. A nd orbital has $n - 3$ nodes, so again, the first allowed one, $3d$, has none, $4d$ has one, etc. The same pattern holds for higher l orbitals. More nodes as n and l increase is to be expected, since this means higher kinetic energy and leads to a higher total energy. This node structure can be understood to be necessarily this way because of the orthogonality between different eigenfunctions (maybe we'll belabour this point a bit more in class).

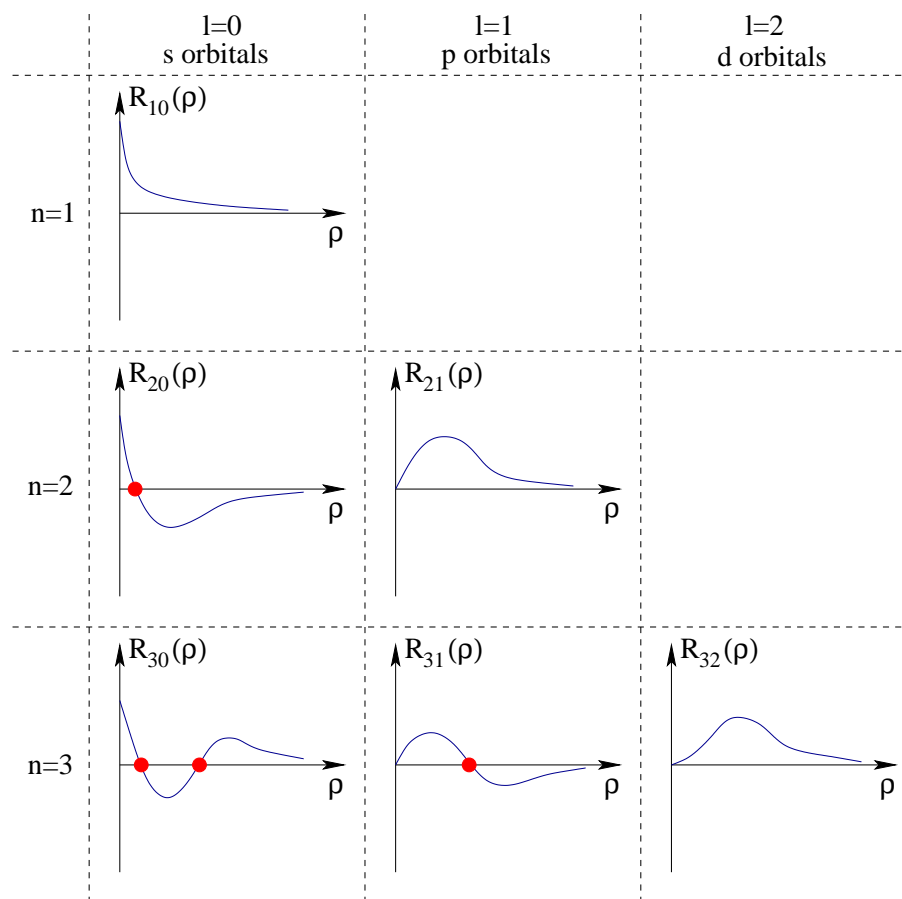


Figure 2: Sketch of the shape of the first few radial functions $R_{nl}(\rho)$.

(iii) for a given n , as l increases orbitals spread farther out from the origin (not surprising, if you remember that l characterizes angular momentum, and you'd expect a state with more angular momentum to be farther out). My hand-made sketch is not showing this very well, so have a look at the better plots online.

So, the $R_{nl}(\rho)$ tells us how the wavefunction decreases as you go away from the origin, in any direction. But this is the ρ dependence, how about the r dependence? Well, they are proportional, but the proportionality constant depends on both Z and n . The trends are:

- for a fixed n , the larger Z is, the “smaller” is the orbital, and of course the more negative is the energy E_n . Not surprising, really, since larger Z means stronger attraction, so all else being equal the electron should be closer to the nucleus and have lower energy (more strongly bound).
- for a fixed Z , the larger n is, the more spread-out is the orbital, and of course the less negative is the energy E_n . Not surprising, either. We know different orbitals are orthogonal, so if the ones with low n occupy the space close to the nucleus, the ones with higher n are pushed further out. The electron feels less attraction there, so its energy goes up.

The $Y_{lm}(\theta, \phi)$ part (these are **spherical functions**) tells us the angular dependence of the wavefunction, as you stay at any fixed r and move around the surface at that sphere. These are again simple functions, which also split into a part depending only on θ times a simple exponential $e^{im\phi}$.

More specifically, $Y_{00}(\theta, \phi) = \text{const}$, meaning that all s orbitals are spherically symmetric, looking precisely the same in any and all direction. You can think of “s” as standing for “sphere”.

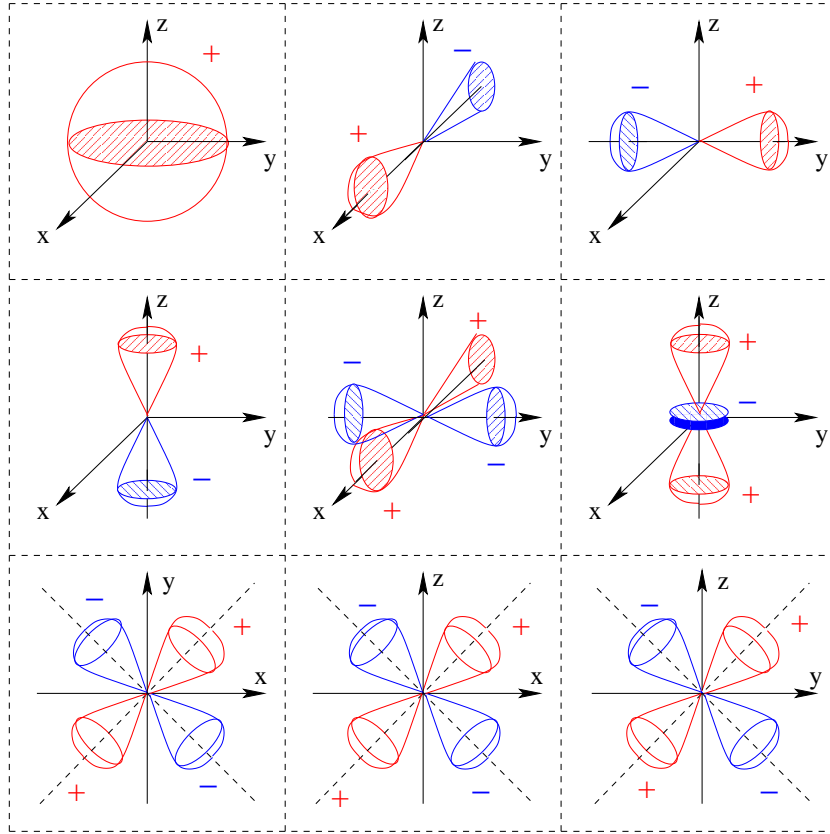


Figure 3: Sketch of angular dependence for s , p and d orbitals.

For $l = 1$, we have, up to normalization constants: $Y_{1,-1}(\theta, \phi) \propto \sin \theta e^{-i\phi}$; $Y_{1,0}(\theta, \phi) \propto \cos \theta$; $Y_{1,+1}(\theta, \phi) \propto \sin \theta e^{i\phi}$. These are complex functions, obviously. Dealing with real functions is easier, and since these functions are degenerate, we are free to make any linear combinations and they are still eigenfunctions. Using $e^{\pm i\phi} = \cos \phi \pm i \sin \phi$, we can make 3 orthogonal but real combinations:

$$p_x(\theta, \phi) = \frac{1}{\sqrt{2}} (Y_{1,-1}(\theta, \phi) + Y_{1,+1}(\theta, \phi)) \propto \sin \theta \cos \phi = \frac{x}{r}$$

$$p_y(\theta, \phi) = \frac{i}{\sqrt{2}} (Y_{1,-1}(\theta, \phi) - Y_{1,+1}(\theta, \phi)) \propto \sin \theta \sin \phi = \frac{y}{r}$$

$$p_z(\theta, \phi) = Y_{1,0}(\theta, \phi) \propto \cos \theta = \frac{z}{r}$$

These are the famous p orbitals, which you've probably encountered before. Clearly, p_x is mostly concentrated along the x axis, and is positive for $x > 0$ and negative for $x < 0$. It quickly vanishes as you move off x -axis, and this is what the sketches above are trying to suggest. Similarly, p_y and p_z look like "lobes" with opposite signs, oriented along their respective axes.

You can see right away that even if they have the same energy, electrons occupying different orbitals can have very different spatial distributions. While an s electron is equally likely to be found anywhere around the nucleus, a p_x electron will be very likely along the x axis and very unlikely to be found anywhere else, etc. This will have major consequences for chemistry, as we will see in a bit.

Before moving on, let me also comment on the d orbitals $l = 2$. Again, you can easily find the formulae for the $Y_{2,m}$ functions, but instead of working with these complex functions, it is convenient

to make linear combinations which are real. These lead to the so-called d orbitals, whose names basically tell you what their angular dependence is (so, no need to memorize):

$$\begin{aligned}
 d_{xy}(\theta, \phi) &\propto \frac{xy}{r^2} = \sin^2 \theta \sin \phi \cos \phi \\
 d_{xz}(\theta, \phi) &\propto \frac{xz}{r^2} = \sin \theta \cos \theta \cos \phi \\
 d_{yz}(\theta, \phi) &\propto \frac{yz}{r^2} = \sin \theta \cos \theta \sin \phi \\
 d_{x^2-y^2}(\theta, \phi) &\propto \frac{x^2 - y^2}{r^2} = \sin^2 \theta (\cos^2 \phi - \sin^2 \phi) = \sin^2 \theta \cos(2\phi) \\
 d_{3z^2-r^2}(\theta, \phi) &\propto \frac{3z^2 - r^2}{r^2} = 3 \cos^2 \theta - 1
 \end{aligned}$$

What do they look like? Well, consider d_{xy} . It is clearly zero for both $x = 0$ and $y = 0$, and it is maximum when both are as large as possible, i.e. along the $x = \pm y$ diagonals (but the sign changes). It also lies in the xy plane – if you go to large z while keeping r constant (remember, we are on the surface of a sphere) then x and y decrease and d_{xy} vanishes. Similar thinking should lead to figure out the shapes of the other d orbitals, and see if you agree with my sketches on the previous page.

So, these are the eigenenergies and eigenfunctions of the one-electron case. H only has one electron so it is perfectly described by this for $Z = 1$, therefore in the ground-state its electron goes in the $1s$ shell, either with spin-up or spin-down. The electronic configuration of H is, therefore $1s^1$ (the little upper script shows how many electrons are in that orbital). He has 2 electrons, so clearly its electronic structure is $1s^2$ (the second electron goes into the lowest orbital available to it).

What happens with Li, $Z = 3$? Clearly, the 3rd electrons must go into a $n = 2$ orbital. According to what we just discussed, $2s$ and $2p$ should have equal energy so either $2s$ or $2p$ should be just as good – however that was true only if there is a single electron in the system. Here, we already have two electrons filling the $1s$ shell, basically putting themselves between the nucleus and this outer, 3rd electron. This process is known as **shielding**, or **screening**. While calculating precisely its effect is a very difficult enterprise, we can infer the qualitative trend quite easily. First, the two inner electrons fill a spherical shell, so the spherical symmetry of the problem remains (in some sense, it's as if the total attractive charge experienced by the 3rd outer electron has gone down to $Z - 2$). This is why we should expect that the $n = 2$ orbitals should have similar shapes as in the single-electron case. However, because s orbitals have a finite overlap with the nucleus, while the p orbitals are pushed further out, it follows that s orbitals are somewhat less effectively screened (they feel more attraction from the nucleus) and should have a lower energy. By contrast, the p orbitals will have higher energy. This is true not just for $n = 2$ and not just for s and p orbitals, but in general. Inner electrons partially shield the attraction for all electrons in a higher n level, but less so for s , more for p , even more for d etc.

This is why because of electron-electron interactions, $E_{ns} < E_{np} < E_{nd} < \dots$. These energies are sketched in Fig 4, where the spectrum of the one-electron ion is compared to that of the many-electron atom. Note that the energy of $3d$ levels is pushed above that of $4s$ ones, and there are a few other such cases where levels with low l and high n lie below levels with lower n but higher l .

Now we know all we need to understand the periodic table. As already stated, H and He have only $n = 1$ orbitals filled, hence they are on the first line (see leftmost index in the table).

The $n = 2$ orbitals start being filled when we start the second line. First is Li with $1s^2 2s^1$, since $E_{2s} < E_{2p}$, then Be with $Z = 4$, $1s^2 2s^2$, and then the next 6 elements which fill the $2p$ orbitals one

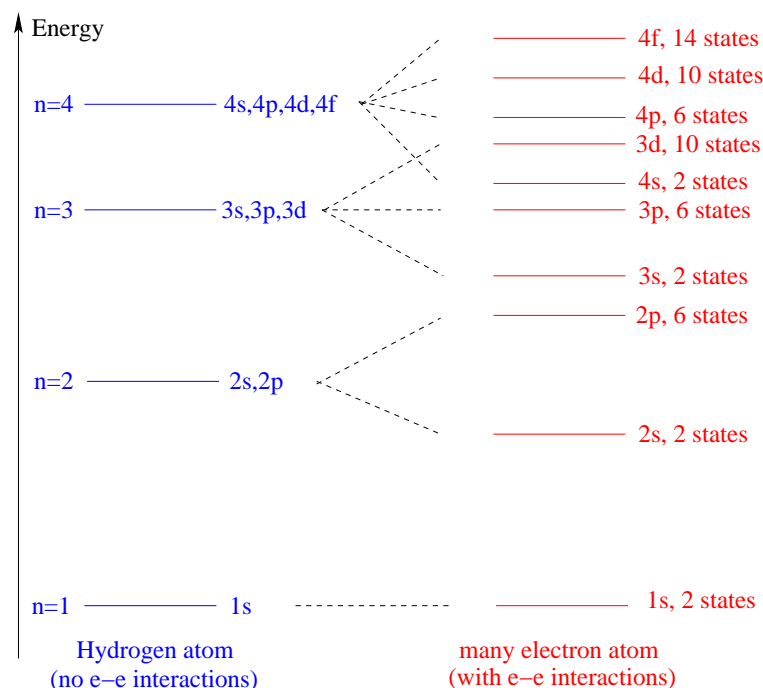


Figure 4: Sketch of the spectrum of the single-electron ion (left) and of the many-electron atom (right). Some of the degeneracies are lifted in the latter case because of electron-electron interactions.

by one. You can now see that the integers listed to the right of each element's box are precisely these occupation numbers, giving their electronic structure.

We then start the 3rd line with $n = 3$ orbitals being filled, first the $3s$ and then the $3p$. However, because $E_{3d} > E_{4s}$, instead of continuing with 10 more elements on this line, with $3d$ levels being filled, instead we start the 4th line, fill its $4s$ orbitals first, and then insert the 10 elements having partially filled $3d$ shell. After which we finish with the 6 elements with $4p$ shell partially filled. This explains the insertions of the 4 additional pieces in lines $n = 4 - 7$, to accommodate electrons in the $(n - 1)d$ orbitals. Two more additional insertions occur for the $4f, 5f$ orbitals, which also are located out of their turn, since for eg $E_{6s} < E_{4f} < E_{5d} < E_{4p}$.

In case you're wondering what happens when a p or a d is partially filled, let's look at N with $1s^2 2s^2 2p^3$. It turns out to have one electron each into of the $2p_x, 2p_y$ and $2p_z$ orbitals, as opposed to two in the same orbital but with opposite spins. This is so as to keep them away from each other to limit their repulsions, which raise the energy (remember that each p orbital points in a different direction). Turns out that these 3 electrons also have their spins parallel, either all up, or all down. We can also understand this as a way to lower the repulsion. The wavefunction must be antisymmetric when we exchange any two fermions. If all have the same spin, then the spin part of the wavefunction is symmetric and the radial part must be antisymmetric. From $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = -\psi(\vec{r}_2, \vec{r}_1, \vec{r}_3)$ etc, it follows that the wavefunction vanishes if $\vec{r}_1 = \vec{r}_2$ etc (Pauli's principle, really - can't have two electrons with the same spin, at the same position). So they're never too close together, meaning that their repulsions are not too big. In contrast, if electrons had different spins they could go to the same location and that would increase the repulsion; that can't be the most favorable situation.

These rules about the order in which degenerate orbitals are filled are known as **Hund's rules**. What I just said is the main one (first fill different orbitals with the same spin). You'll learn the remaining bits and pieces in a more advanced course.

All these facts have several interesting consequences. First, this explains why elements in the same **group** (same column) have very similar chemical properties. For example, all elements in group 1 have a single valence electron in the last occupied ns shell, all elements in group 2 have 2 valence electrons in the last occupied ns shell, etc – and since these are the outermost ones spatially, they are the electrons that will determine how the element interacts with other elements. These outer electrons are known as **the valence electrons**.

From these facts we can also infer the trends for the **atomic radius** of the atom, which basically tells us roughly how far away from the nucleus are the valence electrons. As we go along a line in the periodic table with a given n and put in atoms with increasing Z , this tells us that their atomic radius must decrease steadily (see discussion for $R_{nl}(r)$). This is indeed true, as shown by table 2.9 in Nick's notes, which lists these values. He also discusses a couple of special cases to this general trend (basically, when we insert the elements with a different n , lower in the table). The atomic radius also increases steadily as you move down in a column, simply because one has to put the valence electrons in levels with higher n , which are more spread-out.

Next is the **ionization energy**, which is the minimum energy needed to remove one electron from the atom. This is expected to increase as you move to right along each line, since to remove one of the least expensive electrons, the valence electrons, you need to pay E_{nl} energy. For a fixed n, l this increases with Z , showing that it's much harder to take an electron away from F than from O or any other of the elements to its left. As you go down in a column, this ionization energy decreases because of the shielding, as discussed – outer electrons are less difficult to remove (takes less energy). These expectations are confirmed by table 2.10 in Nick's notes, where the measured values for ionization energies are listed. He also discusses a couple of exceptions to these rules.

There is also an **electron affinity** – this tells us by how much the energy of the atom is lowered if you give it an extra electron to turn it into a negatively charged ion. These values are shown in Table 2.11 of Nick's notes. To understand this properly, let's start with the **noble gases** which occupy group 8 and have filled n shells. An extra electron would go in the $(n+1)s$ shell and would lower the energy by $E_{(n+1)s}$; but it also experiences more repulsion from the other electrons than in a neutral atom. Turns out the two nearly cancel out, which is why their affinity is zero – they don't really want an extra electron. This is what makes the elements of group 8 be known as "noble" : they don't want to accept extra electrons but it is very hard to remove one of the ones they have (very high ionization energy) – so they basically don't interact chemically with any other elements.

In contrast, elements from group 7 have high electron affinity, because for them it is energetically very convenient to get one more electron to fill their outer shell to become very stable. The electron affinity decreases as you move to the left, as you would expect. The decrease is not monotonic. The affinity goes to zero (or very near) every time a subshell is also filled, and then increase again to the left of that. If you're interested in more details, see Nick's notes. For what we need in the following, knowing these qualitative facts and trends should suffice.