Atomic structure and atomic spectra
II. The structure of many-electron atoms

The Schrödinger equations for many-electron atoms are extremely complicated because all the electrons interact with each other. Even in the case of the He atom, with its two electrons, no analytical expression for the orbitals and energies can be derived, and we are forced to make approximations. We shall adopt a simple approach based on what we already know about the structure of hydrogenic atoms.

The orbital approximation

The actual wavefunction of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it as $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...)$. However, in the **orbital approximation** we suppose that a reasonable first approximation to this exact wavefunction is obtained by assuming that each electron occupies its 'own' orbital:

$$\psi(r_1, r_2, \ldots) = \psi(r_1)\psi(r_2)\ldots$$

We can think the individual orbitals resemble the hydrogenic orbitals, but with nuclear charges that are modified by the presence of all the other electrons in the atom. This description is only approximate, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

The helium atom

The orbital approximation allows us to express the electronic structure of an atom by specifying its **configuration**, the list of occupied orbitals (usually, but necessarily, in its ground state). Thus, as the ground state of a hydrogenic atom consists of the single electron in a 1s orbital, we report its configuration as $1s^1$.

The He atom has two electrons. We can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a 1s hydrogenic orbital, but since $Z = 2$ it is more compact than in H itself. The second electron joins the first in the 1s orbital, and so the electron configuration of the ground state of He is $1s^2$.

The Pauli principle

Lithium, with $Z = 3$, has three electrons. The first two occupy a 1s orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not joined the first two in the 1s orbital since that configuration is forbidden by the **Pauli exclusion principle**.

No more than two electrons may occupy any given orbital, and if two do occupy one orbital, their spins must be paired.

Electrons with paired spins, which are denoted as $\uparrow\downarrow$, have zero net spin angular momentum since the spin angular momentum of one electron is cancelled by the spin of the other. This remarkable principle is the key to the structure of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by Wolfgang Pauli in 1924 when he was trying to account for the absence of some lines in the spectrum of helium.

The Pauli exclusion principle applies to any pair of identical **fermions**, or particles with half-integer spin. Thus it applies to electrons, protons, neutrons, an ^{13}C nuclei (all of which have spin 1/2) and to ^{35}Cl nuclei (which have spin 3/2). It does not apply to identical **bosons**, or particles with integer spin, which include photons (spin 1) and ^{12}C nuclei (spin 0).

The Pauli exclusion principle is a special case of a general principle called the **Pauli principle**:

When the labels of any two identical fermions are exchanged, the total wavefunction changes sign. When the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

By 'total wavefunction' we mean the entire wavefunction, including the spin of the particles. Let us consider the wavefunction for two electrons $\psi(1,2)$, which is a function of six variables, three the coordinates of electron 1 and three the coordinates of electron 2. The Pauli principle implies it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function:

$$\psi(1,2) = -\psi(2,1)$$

The connection of this general form of the principle with the exclusion principle can be illustrated by the following argument, which has three stages.

An electron we might label 1 in a hydrogenic atom has a wavefunction that is the solution of the Schrödinger equation

$$H_1\psi(1) = E_1\psi(1)$$

An electron we might label 2 in a hydrogenic atom has a wavefunction that is the solution of

$$H_2\psi(2) = E_2\psi(2)$$

When both electrons are present in the same atom,

$$H = H_1 + H_2 + V(1,2) \qquad V(1,2) = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

V is the potential energy of repulsion between the electrons. The wavefunction for the pair of electrons is the solution of $H\psi = E\psi$

As a first approximation we can ignore the repulsion, then the total hamiltonian is $H = H_1 + H_2$, and the solution of the corresponding Schrödinger equation is the product $\psi(1)\psi(2)$ of the individual wavefunctions:

$$H\psi = (H_1 + H_2)\psi(1)\psi(2) = \{H_1\psi(1)\}\psi(2) + \psi(1)\{H_2\psi(2)\}$$

$$= \{E_1\psi(1)\}\psi(2) + \psi(1)\{E_2\psi(2)\} = (E_1 + E_2)\psi(1)\psi(2) = E\psi$$

where $E = E_1 + E_2$. That is the product $\psi(1)\psi(2)$ is an eigenfunction of the simplified hamiltonian H.

To apply the Pauli principle, we must deal with the total wavefunction, the wavefunction including spin. There are four states for two spins:

both α denoted $\alpha(1)\alpha(2)$, both β denoted $\beta(1)\beta(2)$, one α, the other β, denoted $\alpha(1)\beta(2)$ or $\beta(1)\alpha(2)$.

Since we cannot tell which electron is α and which is β, in the last case it is appropriate to express the spin states as the linear combinations

$$\sigma_+(1,2) = \alpha(1)\beta(2) + \beta(1)\alpha(2) \qquad \sigma_-(1,2) = \alpha(1)\beta(2) - \beta(1)\alpha(2)$$

because these allow one spin to be α and the other β with equal probability. The total wavefunction of the system is therefore the product of the orbital part $\psi(1)\psi(2)$ and one of the four spin states:

$$\psi(1)\psi(2)\alpha(1)\alpha(2) \qquad \psi(1)\psi(2)\beta(1)\beta(2)$$
$$\psi(1)\psi(2)\sigma_+(1,2) \qquad \psi(1)\psi(2)\sigma_-(1,2)$$

Now we take into account the Pauli principle. It says that if a wavefunction is to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ to $\psi(2)\psi(1)$, which is the same. The same is true for $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed because they don't change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = \alpha(2)\beta(1) + \beta(2)\alpha(1) = \sigma_+(1,2)$$

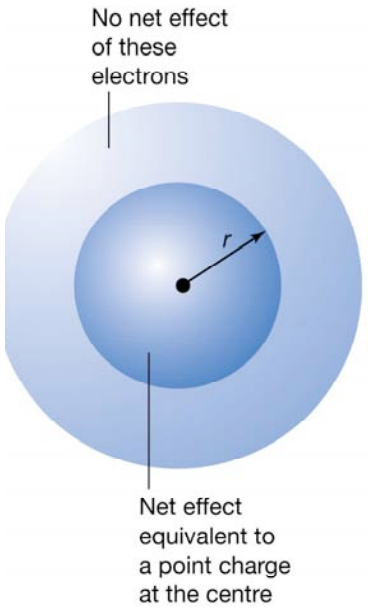
because it is simply the original written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$

$$\sigma_-(2,1) = \alpha(2)\beta(1) - \beta(2)\alpha(1) = -\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_-(1,2)$$

and so it does change sign (it is 'antisymmetric'). Therefore, the product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has one α, and one β spin. This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the electron are different, and both electrons may then have (but need not have) the same spin. Nevertheless, even then the overall wavefunction must still be antisymmetric overall, and must satisfy the Pauli principle itself.

In the case of Li (Z = 3), the third electron cannot enter the 1s orbital because that orbital is already full: we say the K shell is **complete** and that the two electrons form a **closed shell**. Since the same closed shell occurs in the He atom, we denote it [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is the one with n = 2 and hence belonging to the L shell. However, now we have to decide whether the next available orbital is the 2s orbital or a 2p orbital, and therefore whether the lowest energy configuration of the atom is $[He]2s^1$ or $[He]2p^1$.



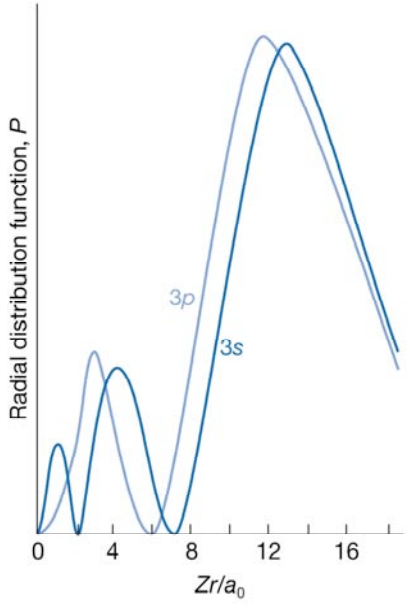
Penetration and shielding

Unlike in hydrogenic atoms, the 2s and 2p orbitals (and, in general, all subshells of a given shell are not degenerate in many-electron atoms. s electrons generally lie lower in energy than p electrons of a given shell, and p electrons lie lower than d electrons. An electron in a many-electron atom experiences a coulombic repulsion from all other electrons present. If it is at an average distance r from the nucleus, it experiences an average repulsion that can be represented by a point negative charge located at the nucleus and equal in magnitude to the total charge of the electrons within a sphere of radius r.

The effect of this point charge is to reduce the full charge of the nucleus from Ze to $Z_{eff}e$, where Z_{eff} is the **effective atomic number**. We say that the electron experiences a **shielded** nuclear charge, and that the true atomic number is reduced to Z_{eff} by an amount called the **shielding constant** σ:

$$Z_{eff} = Z - \sigma$$

The electrons do not actually 'block' the full coulombic attraction of the nucleus: the effective charge is simply a way of expressing the *net* outcome of the nuclear attraction and the electronic repulsions in terms of a single equivalent charge at the center of the atom.



The effective atomic number is different for s and p electrons because they have different radial wavefunctions. An s electron has a greater **penetration** through inner shells than a p electron in the sense that it is more likely to be found closer to the nucleus than a p electron of the same shell (remember that p orbital has a node at the nucleus). Since only electrons inside the sphere defined by the location of the electron (in effect, the core electrons) contribute to shielding, an s electron experiences less shielding than a p electron and therefore experiences a larger Z_{eff}. Consequently, by the combined effects of penetration and shielding, an s electron is more tightly bound than a p electron of the same shell. Similarly, a d electron penetrates less than a p electron of the same shell, and therefore experiences more shielding and an even smaller Z_{eff}.

Effective atomic numbers of different types of electrons in atoms have been calculated from their wavefunctions (obtained by numerical solution of the Schrödinger equation for the atom):

	He 1s	Na 1s	Na 2s	Na 2p	Na 3s
Z_{eff}	1.69	10.6	6.85	6.85	2.20

We see that in general s electrons do experience higher effective atomic numbers than p electrons, although there are some discrepancies.

The consequence of penetration and shielding is that the energies of subshells in a many-electron atom in general lie in the order: **s < p < d**

The individual orbitals of a given subshell (such as the three p orbitals of the p subshell) remain degenerate since they all have the same radial characteristics and so experience the same effective nuclear charge.

Completing the Li story, since the shell with $n = 2$ consists of two nondegenerate subshells, with the 2s orbital lower in energy than the three 2p orbitals, the third electron occupies the 2s orbital. This results in the ground state configuration $\mathbf{1s^2 2s^1}$, with the central nucleus surrounded by a complete helium-like shell of two 1s electrons, and around that a more diffuse 2s electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** since they are largely responsible for the chemical bonds that the atom forms. Thus, the valence electron in Li is a 2s electron and its other two electrons belong to its core.

The building-up principle

The extension of the procedure used for H, He, and Li to other atoms is called the **building-up principle**, or the **Aufbau principle**, from the German word for building up. The aim of the building-up principle is to find an order of occupation of the hydrogenic orbitals that leads to the ground state configuration of the neutral atom.

We imagine the bare nucleus of atomic number Z, and then feed into orbitals Z electrons in succession. The order of occupation is

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s

and each orbital may accommodate up to two electrons. This order of occupation is *approximately* the order of energies of the individual orbitals, since in general the lower the energy of the orbital, the lower the total energy of the atom as a whole when that orbital is occupied. However, there are complicating effects arising from electron-electron repulsions that are important when the orbitals have very similar energies (such as the 4s and 3d orbitals near Ca and Sr) and one must take special care then.

We feed the Z electrons in succession into the orbitals subject to the demand of the exclusion principle that no more than two can occupy any single orbital. Since an s subshell consists of only one orbital, up to two electrons may occupy it. Since the p subshell consists of three orbitals, it can accommodate up to 6 electrons; the d subshell, which consists of five orbitals, can accommodate up to 10 electrons:

Carbon $Z = 6$: $1s^2 2s^2 2p^2$ or $[He]2s^2 2p^2$ or $[He]\ 2s^2 2p_x^{\ 1} p_y^{\ 1}$

Nitrogen $Z = 7$: $1s^2 2s^2 2p^3$ or $[He]2s^2 2p^3$ or $[He]\ 2s^2 2p_x^{\ 1} p_y^{\ 1} p_z^{\ 1}$

On electrostatic grounds we can expect that the last two electrons for C (or three for N) occupy different 2p orbitals since they will then be further apart on average and repel each other less than if they were in the same orbital. The same rule applies whenever degenerate orbitals of a subshell are available for occupation:

Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

An additional question arises when electrons occupy orbitals singly, for there is then no requirement that their spins should be paired. We need to know whether the lowest energy is achieved when the electron spins are the same (both α, for instance, denoted $\uparrow\uparrow$, if there are two electrons involved, as in C) or when they are paired ($\uparrow\downarrow$). The answer is the **Hund's rule**:

An atom in its ground state adopts a configuration with the greater number of unpaired electrons.

The explanation of Hund's rule is complicated, but it reflects the quantum mechanical property of **spin correlation**, that electrons with parallel spins have a tendency to stay well apart and hence repel each other less. The effect of spin correlation is to allow the atom to shrink slightly, so the electron-nucleus interaction is improved when the spins are parallel.

We can now conclude that in the ground state of the carbon atom, the two 2p electrons have the same spin, and that the two 2p electrons in different orbitals in the O atom ([He] $2s^2 2p_x^2 p_y^1 p_z^1$) have the same spin (the two in the $2p_x$ orbital are necessarily paired).

Neon, with $Z = 10$, has the configuration $[He]2s^2 2p^6$, which completes the L shell. This closed-shell configuration is denoted [Ne], and acts as a core for subsequent elements. The next electron must enter the 3s orbital and begin a new shell, and so an Na atom, with $Z = 11$, has the configuration $[Ne]3s^1$. Like lithium with the configuration $[He]2s^1$, sodium has a single s electron outside a complete core.

This analysis has brought us to the origin of chemical periodicity. The L shell is completed by eight electrons, and so the element with $Z = 3$ (Li) should have similar properties to the element with $Z = 11$ (Na). Likewise, Be ($Z = 4$) should be similar to $Z = 12$ (Mg), and so on up to the noble gases He ($Z = 2$), Ne ($Z = 10$), and Ar ($Z = 18$).

Argon has complete 3s and 3p orbitals, and as the 3d orbitals are high in energy it counts as having a closed-shell configuration. Indeed, the 3d orbitals are so high in energy that the next electron (for K) occupies the 4s orbital and the K atom resembles a Na atom. The same is true for a Ca atom, which has the configuration $[Ar]4s^2$. However, at this point, the 3d orbitals become comparable in energy to the 4s orbitals, and they start to be filled.

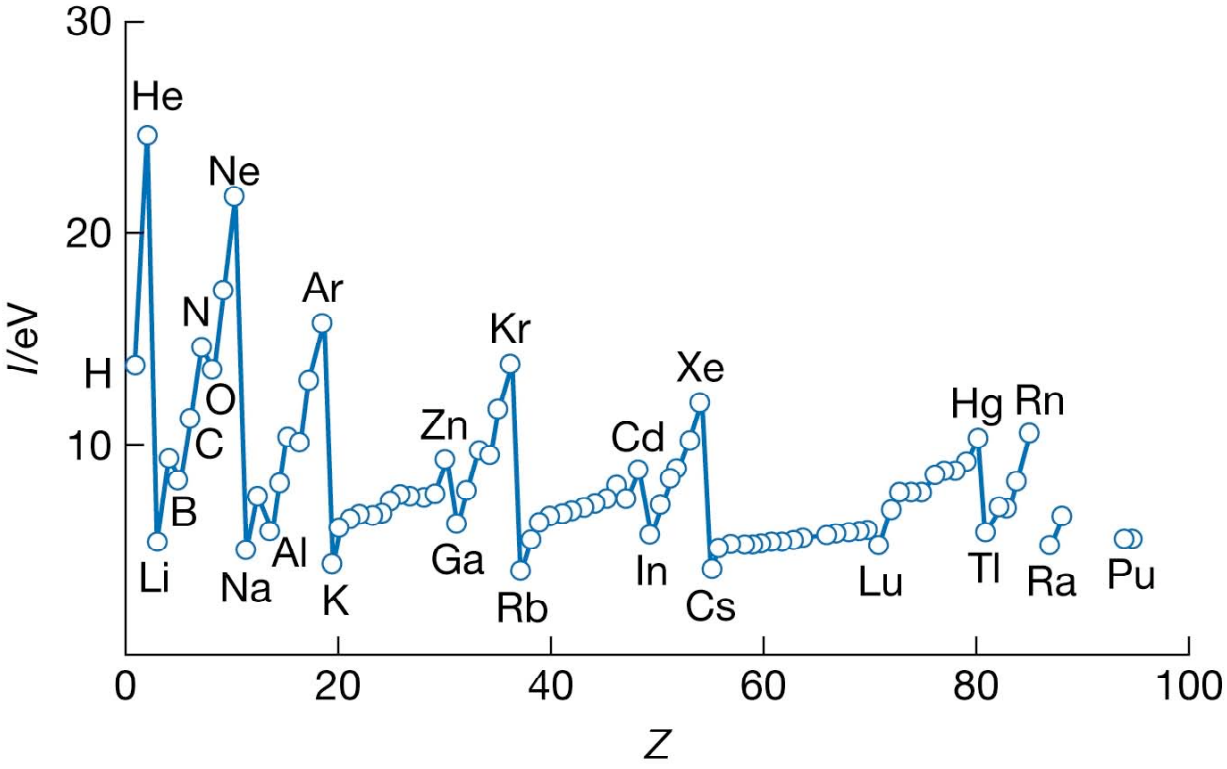
Ten electrons can be accommodated in the five 3d orbitals, which accounts for the electron configurations of scandium to zinc. However, the building-up principle has less clear-cut predictions about the ground state configurations of these elements because electron-electron repulsions are comparable to the energy difference between the 4s and 3d orbitals, and a simple analysis no longer works. At gallium, the energy of the 3d orbitals has fallen so far below those of the 4s and 4p orbitals that the 3d orbitals can be largely ignored, and the building-up principle can be used the same way as in preceding periods. The 4s and 4p subshells constitute the valence shell, and period terminates at Kr.

Since 18 electrons have intervened since argon, this period is the first **long period** of the periodic table. The existence of the d-block elements (the transition metals) reflects the stepwise occupation of the 3d orbitals, and the subtle shades of energy differences along this series gives rise to the rich complexity of inorganic d-metal chemistry. A similar intrusion of the f orbitals in Periods 6 and 7 accounts for the existence of the f block of the periodic table (the lanthanides and actinides).

We derive the configurations of cations of elements in the s, p, and d blocks of the periodic table by removing electrons from the ground state configuration of the neutral atom in a specific order. First, we remove p electrons (if any are present), then s electrons, and then as many d electrons as are necessary to achieve the stated charge. For instance, since the configuration of Fe is $[Ar]3d^6 4s^2$, the Fe^{3+} cation has the configuration $[Ar]3d^5$. We derive the configurations of anions simply by continuing the building-up procedure and adding electrons to the neutral atom until the configuration of the next noble gas has been reached. Thus, the configuration of the O^{2-} ion is achieved by adding two electrons to $[He]2s^2 2p^4$, giving $[He]2s^2 2p^6$, the analogue of Ar configuration.

The periodicity of ionization energies

The minimum energy necessary to remove an electron from a many-electron atom is its **first ionization energy** I_1.The **second ionization energy** I_2 is the minimum energy needed to remove a second electron (from a singly-charged cation). Lithium has a low first ionization energy: its outermost electron is well-shielded from the nucleus by the core ($Z_{eff} = 1.3$ compared with $Z = 3$) and it is easily removed.



Berillium has a higher nuclear charge than lithium, and its outermost electron (one of the two 2s electrons) is more difficult to remove: its ionization energy is larger. The ionization energy decreases between beryllium and boron because in the latter the outermost electron occupies a 2p orbital and is less strongly bound than if it had been a 2s electron. The ionization energy increases between boron and carbon because the latter's outermost electron is also 2p and the nuclear charge has increased. Nitrogen has a still larger ionization energy because of the further increase in nuclear charge.

There is then a kink in the curve which reduces the ionization energy of oxygen below what would be expected by simple extrapolation. This is because at oxygen a 2p orbital must become doubly occupied, and the electron-electron repulsions are increased above what would be expected by simple extrapolation along the row. The kink is less pronounced in the next row, between phosphorus and sulfur, because their orbitals are more diffuse. The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the nucleus for the outermost electrons.

The outermost electron in sodium is 3s. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core. As a result, the ionization energy of sodium is substantially lower than that for neon. The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

Self-consistent field orbitals

The central difficulty of the Schrödinger equation is the presence of the electron-electron interaction terms:

$$V = \frac{e^2}{4\pi\varepsilon_0} \sum_{\substack{i,j \\ pairs}} \frac{1}{r_{ij}}$$

r_{ij} is the separation of electrons i and j, and the sum is over all pairs of electrons. It is hopeless to expect to find analytical solutions of this Schrödinger equation. But computational techniques are available that give very detailed and reliable numerical solutions for the wavefunctions and energies. The techniques were originally introduced by Douglas Hartree (before computers were available) and then modified by Vladimir Fock to take into account the Pauli principle correctly. In broad outline, the **Hartree-Fock procedure** is as follows.

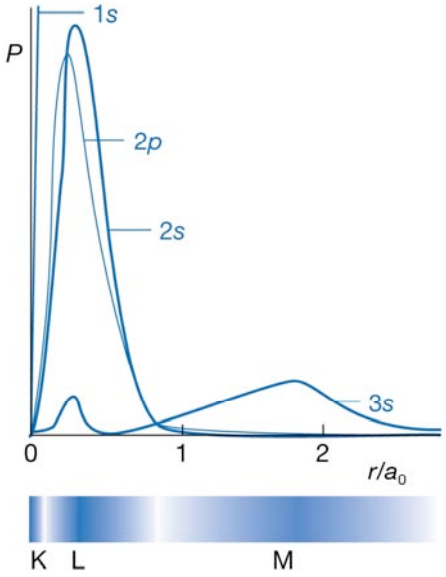
Imagine we have a rough idea of the structure of the atom. In the Na atom, for instance, the orbital approximation suggests the configuration $1s^2 2s^2 2p^6 3s^1$ with the orbital approximated by hydrogenic atomic orbitals. Now consider the 3s electron. A Schrödinger equation can be written for this electron by ascribing to it a potential energy that arises from the nuclear attraction and the average electronic repulsion from the other electrons in their approximate orbitals.

This equation has the form

$$\frac{-\hbar^2}{2m_e}\nabla^2\psi_{3s} - \frac{Ze^2}{4\pi\varepsilon_0}\psi_{3s} + V_{ee} = E\psi_{3s}$$

where V_{ee} which depends on the wavefunctions of all the other electrons, is the average repulsion term. The equation may be solved for ψ_{3s} (by numerical integration), and the solution obtained will be different from the solution guessed earlier.

The procedure is then repeated for another orbital, such as 2p. The Schrödinger equation is written in a form like before but with the improved 3s orbital used in setting up the electron-electron repulsion term. The equation is then solved, giving an improved version of 2p. This procedure is repeated for the 2s and 1s orbitals, each time using the improved orbitals found at the earlier stage. The whole procedure is repeated using the improved orbitals, and a second improved set of orbitals is obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the latest cycle. The solutions are then **self-consistent** and accepted as final.



Some of the self-consistent field (SCF) Hartree-Fock (HF) atomic orbitals (AO) are shown in the Figure. They show the grouping of electron density into shells (note that the 3s orbital lies outside the inner *K* and *L* shells), as was anticipated by the early chemists, and the differences of penetration. These SCF calculations therefore support the qualitative discussion by providing detailed wavefunctions and precise energies.

The spectra of complex atoms

The spectra of atoms become very complicated as the number of electrons increases, but there are some important and moderately simple features. The general idea is straightforward: lines in the spectrum (in either emission or absorption) occur when the atom undergoes a change of state with a change of energy ΔE, and emits or absorbs a photon of frequency $\nu = \Delta E/h$ and wavenumber $\nu/c = \Delta E/h/c$. Hence, we can expect the spectrum to give information about the energies of electrons in atoms. However, the actual energy levels are not given solely by the energies of the orbitals, because the electrons interact with each other in various ways.

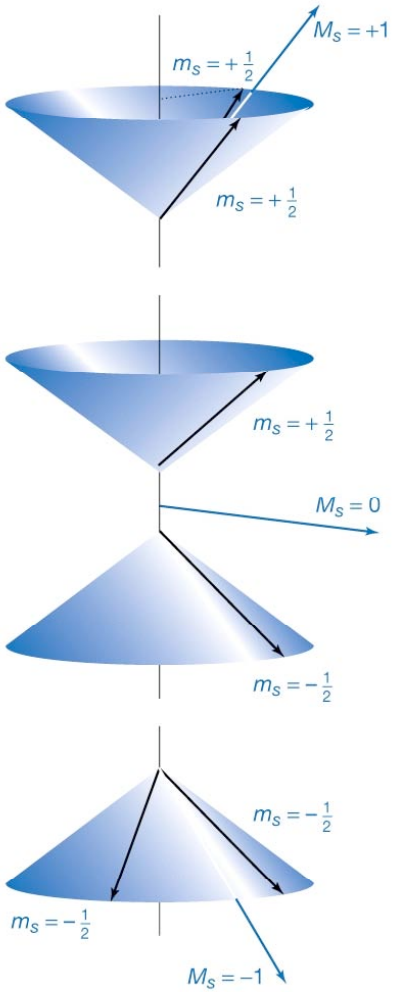
Quantum defects and ionization limits

Atomic spectroscopy can be applied to determine ionization energies. However, the procedure for many-electron atoms is more complicated than for a hydrogenic atom because the energy levels of a many-electron atom do not in general vary as $1/n^2$. The outermost electrons experience as a result of penetration and shielding a nuclear charge of slightly more than $1e$ because in a neutral atom the other $Z - 1$ electrons cancel all but about one unit of nuclear charge. Typical values of Z_{eff} are a little more than 1, so we expect the binding energies to be given by $-hcR/n^2$, but slightly lower in energy than this formula predicts. Therefore, we introduce a **quantum defect**, δ, and write the energy as $-hcR/(n-\delta)^2$. The quantum defect is regarded as a purely empirical quantity.

There are some excited states that are so diffuse (meaning that one electron is very far from the rest and the nucleus) that the $1/n^2$ variation is valid: these states are called **Rydberg states**. For such states,

$$\tilde{\nu} = \frac{I}{hc} - \frac{R}{n^2}$$

A plot of wavenumber against $1/n^2$ can be used to obtain I by extrapolation.

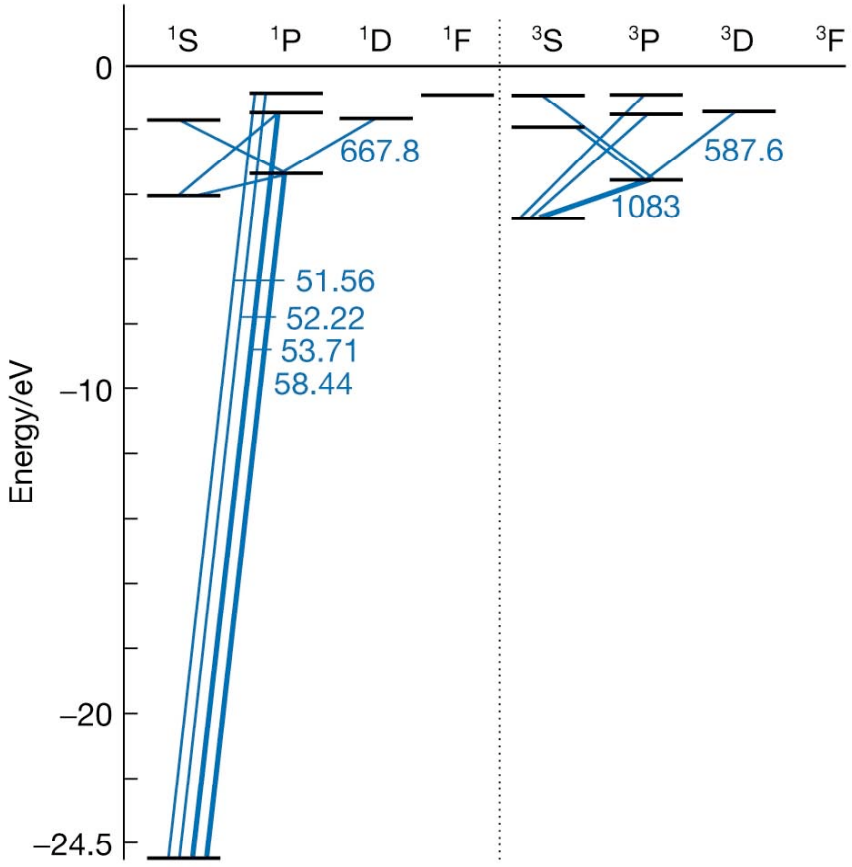


Singlet and triplet states

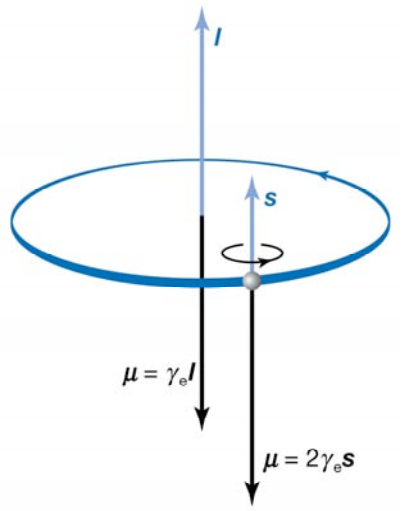
Suppose we were interested in the energy levels of a He atom, with its two electrons. We know that the ground configuration is $1s^2$ and can anticipate that an excited configuration will be one in which one of the electrons has been promoted into a 2s orbital, giving the configuration $1s^12s^1$. The two electrons need not to be paired because they occupy different orbitals.

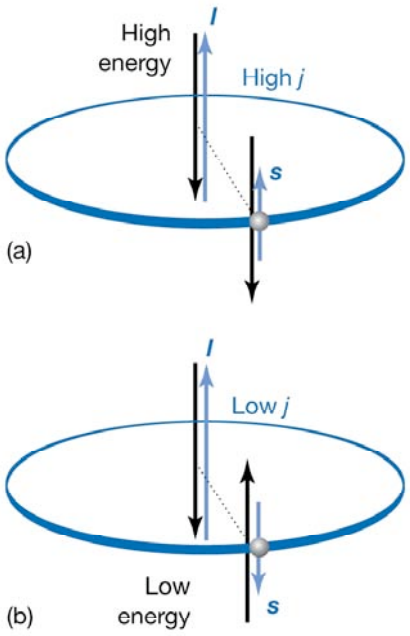
According to Hund's rule, the state of the atom with spins parallel ($\uparrow\uparrow$) lies lower in energy than the state in which they are paired ($\uparrow\downarrow$). Both states are permissible, and can contribute to the spectrum of the atom. The two spin arrangements differ in their overall spin angular momentum. In the paired case, the two spin momenta cancel each other, and there is zero net spin. This paired-spin arrangement is called a **singlet** state. In the parallel case, the two spins add together to give a non-zero total spin and the resulting state is called **triplet**.

The fact that the (↑↑) arrangement of spins in the $1s^1 2s^1$ configuration of the He atom lies lower in energy than the (↑↓) arrangement can now be expressed by saying that the triplet (↑↑) state of the $1s^1 2s^1$ configuration of He lies lower in energy than the singlet (↑↓) state. This is a general conclusion that applies to other atoms (and molecules), and for states arising from the same configuration, the triplet state generally lies lower than singlet. The origin of the energy difference lies in the effect of spin correlation, as we saw in the case of Hund's rule for ground-state configurations. Since the coulombic interaction between electrons in an atom is strong, the difference in energies between singlet and triplet states of the same configuration can be very large. The two states of $1s^1 2s^1$ of He, for instance, differ by $6421\ cm^{-1} = 77\ kJ\ mole^{-1} = 0.80\ eV$.



The spectrum of atomic helium is more complicated than for H. Two simplifying features: the only excited configurations needed to consider are $1s^1 nl^1$ – only one electron is excited. Excitation of two electrons requires an energy greater than the ionization energy of the atom, so He^+ is formed instead of the doubly excited atom. Second – no radiative transitions occur between singlet and triplet states because the relative orientation of two electron spins cannot change during a transition. So, there is a spectrum arising from transitions between singlet states (including the ground state) and between triplet states, but not between the two.





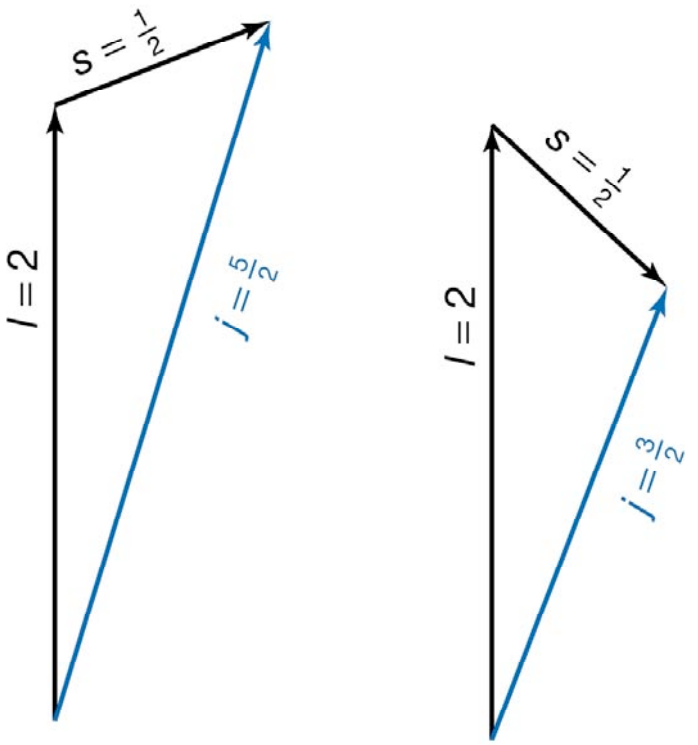
Spin-orbit coupling

The difference in energy between singlet and triplet states stems from the coulombic interaction in combination with the quantum mechanical effect of spin correlation. Another effect stems from *magnetic* interactions of the electrons in atoms. This interaction is weak for light atoms, but for heavy atoms may be comparable to the coulombic interaction and have a marked level on the energy levels of atoms.

Because an electron has spin angular momentum, and because moving charges generate magnetic fields, an electron has a magnetic moment that arises from its spin. Similarly, an electron with orbital angular momentum is in effect a circulating current, an possesses a magnetic moment that arises from its orbital momentum. The interaction of the spin and orbital magnetic moments is called **spin-orbit coupling**. The strength of the coupling, and its effect on the energy levels of the atom, depends on the relative orientations of the spin and orbital magnetic moments and therefore on the relative orientations of the two angular momenta.

The total angular momentum of an electron

Another way of expressing the dependence of the spin-orbit interaction on the relative orientation of the spin and orbital momenta is to say that it depends on the *total* angular momentum of the electron, the vector sum of the spin and orbital momenta.



Thus, when the spin and orbital angular momenta are parallel, the total angular momentum is high; when the two angular momenta are opposed, the total angular momentum is low.

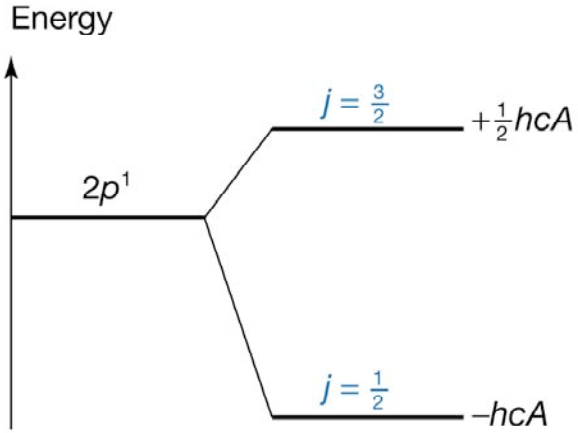
The total angular momentum of a spinning, orbiting electron is quantized. It is described by the quantum numbers j and m_j, with the permitted values of j either $l + 1/2$ (when the two angular momenta are in the same direction) or $l - 1/2$ (when they are opposed). The different levels of j that can arise for a given configurations are called the **levels** of that configuration. For $l = 0$, the only permitted value is $j = s$ (the total angular momentum is the same as the spin angular momentum since there is no other angular momentum in the atom).

Let us, for example calculate the values of the total angular momentum number that may arise from s, p, d, and f electrons with a spin. In each case we must identify the value of l and then two possible values of j:

s electron	$l = 0$	$j = 1/2$
p electron	$l = 1$	$j = 3/2$ and $1/2$
d electron	$l = 2$	$j = 5/2$ and $3/2$
f electron	$l = 3$	$j = 7/2$ and $5/2$

$$E_{l,sj} = \frac{1}{2}hcA\{j(j+1) - l(l+1) - s(s+1)\}$$

The dependence of the spin-orbit interaction on the value of j is expressed in terms of the **spin-orbit coupling** A (in cm^{-1}). A quantum mechanical calculation leads to the formula shown above where the energies of the levels depend on the quantum numbers s, l, and j.



Hence, the different levels of a configuration are split by the spin-orbit coupling and lie at different energies. That being so, we should expect to be able to detect spin-orbit coupling by examining the spectrum of the atom.

Let us calculate the spin-orbit interaction. Assume for example that the spin-orbit interaction constant in the excited $[Ar]5p^1$ configuration of K is 12.5 cm^{-1}. The configuration has $l = 1$ and $s = 1/2$, therefore the two levels are $j = 3/2$ and $j = 1/2$. According to the above formula, the difference in their energies is

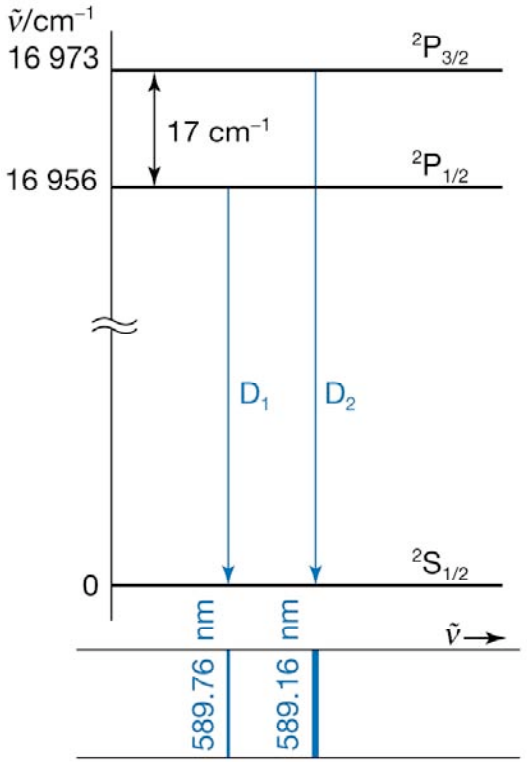
$$\Delta E = hcA\frac{1}{2}\left\{\frac{3}{2}\times\frac{5}{2}-\frac{1}{2}\times\frac{3}{2}\right\} = \frac{3}{2}hcA = 18.8cm^{-1}$$

The fine structure of spectra

We can see the effect of spin-orbit coupling on the states of the atom and its spectrum by considering the alkali metals, which consist of a single valence electron outside a closed core. As a good approximation we can ignore the core electrons (which have no net orbital angular momentum) and concentrate on the valence electron alone.

In the ground state, the valence electron is an s electron, and the $[X]s^1$ configuration (where [X] is a noble gas configuration) has only a single level, $j = 1/2$. Since $l = 0$, the spin-orbit coupling energy is zero (as is confirmed by putting $l = 0$ and $j = s$ in the equation for $E_{l,s,j}$). If the electron is excited into a p orbital, it acquires orbital angular momentum (from the incoming photon), and occupies an orbital with $l = 1$; now the permitted values of j are 3/2 and 1/2 and the $[X]p^1$ configuration has two levels.

The level with $j = 3/2$ corresponds to a state in which the angular momenta (and their magnetic moments) are parallel, and the $j = 1/2$ level is a state in which the angular momenta (and their magnetic moments) are opposed. The former is a high-energy arrangement, and so the level with $j = 3/2$ lies above the level with $j = 1/2$. Therefore, the $[X]p^1$ configuration splits into two levels with $j = 3/2$ above $j = 1/2$. When the excited atom undegoes a transition and the p electron falls into a lower s orbital, two spectral lines are observed, depending on which of the two levels of the $[X]p^1$ configuration was occupied initially. This splitting is called the **fine structure** of the spectrum.



Fine structure can be clearly seen in the emission spectrum from sodium vapor excited by an electric discharge (for example, in one kind of street lightning). The yellow line at 598 nm (17000 cm^{-1}) is actually a doublet – a pair of lines – being composed of two lines at 589.76 nm (16956 cm^{-1}) and 589.16 nm (16973 cm^{-1}).

The transitions are from the $j = 3/2$ and $j = 1/2$ levels of the $[Ne]3p^1$ configuration to the ground configuration $[Ne]3s^1$. Therefore, in Na, the spin-orbit coupling affects the energies by about 17 cm^{-1}. Based on the observed spectrum, we can calculate the spin-orbit-coupling constant for the upper configuration of the Na atom. The splitting in the lines is equal to the splitting of the $j = 3/2$ and 1/2 levels of the excited configuration, which can be expressed in terms of A:

$$\Delta\tilde{\nu} = \frac{1}{2}A\left\{\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)\right\} = \frac{3}{2}A$$

Since the experimental value is 17.2 cm^{-1}, it follows that $A = (2/3)\times 17.2 cm^{-1} = 11.4 cm^{-1}$

The strength of the coupling

The strength of the spin-orbit coupling depends on the nuclear charge. We can understand why this is so by imagining that we are riding on the orbiting electron. We than see a charged nucleus apparently orbiting around us, like the sun rising and setting, and as a result we find ourselves at the center of a ring current. The greater the nuclear charge the greater this current, and therefore the stronger the magnetic field we detect. Since the spin magnetic moment of the electron interacts with this orbital magnetic field, the greater the nuclear charge, the stronger the spin-orbit interaction.

The coupling increases sharply with atomic number (as Z^4), and whereas it is only small in H (giving rise to shifts of energy levels of no more than about 0.4 cm^{-1}), in heavy atoms like Pb it is very large (giving shifts of thousands of cm^{-1}).

Term symbols and selection rules

We have used the expression such as 'the j = 3/2 level of configuration'. A **term symbol**, which is a symbol looking like $^2P_{3/2}$ or $^3D_2$ conveys this information much more succinctly. It also enables us to extend the discussion from a configuration in which there is only one electron of interest (such as the valence electron in the alkali metal atoms) to cases where several electrons must be considered simultaneously, as in alkaline-earth metal atoms.

A term symbol gives three pieces of information:

1) The letter (e.g. P or D in the examples) indicates the *total* orbital angular momentum.

2) The left superscript in the term symbol (e.g. the 2 in $^2P_{3/2}$) gives the **multiplicity** of the term.

3) The right subscript on the term symbol (e.g. 3/2 in $^2P_{3/2}$) is the value of the **total angular momentum quantum number *J***.

We shall now consider what each of these means.

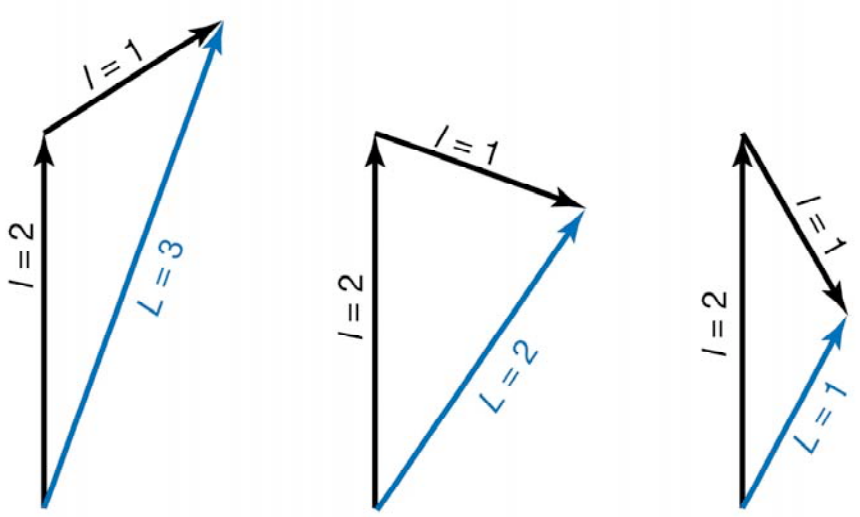
The total orbital momentum

When several electrons are present, it is necessary to judge how their individual orbital angular momenta add together or oppose each other. The **total orbital angular momentum** designated by L is quantized, and like other momenta we have encountered, its magnitude is given by the value of L, and is $\{L(L+1)\}^{1/2}\hbar$. It also has 2 $L + 1$ orientations distinguished by the quantum number M_L, which can take the values L, $L-1$, ..., $-L$.

Similar remarks apply to the total spin S (its orientations are denoted M_S), and the total angular momentum J (with its orientations M_J).

L is obtained by coupling the individual orbital angular momenta using the **Clebsch-Gordan series**:

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$



The maximum value $L = l_1 + l_2$ is obtained when the two orbital angular momenta are in the same direction; the lowest value $|l_1 - l_2|$ is obtained when they are in opposite directions. The intermediate values represent possible intermediate relative orientations of the two momenta.

For two p electrons (for which $l_1 = l_2 = 1$), $L = 2, 1, 0$. The total orbital angular momenta of a p electron ($l_1 = 1$) and a d electron ($l_2 = 2$) correspond to $L = 3, 2, 1$. The code for converting the value of L into a letter is the same as for the s, p, d, f, ... designation of orbitals:

***L*:**	**0**	**1**	**2**	**3**	**4**
	S	**P**	**D**	**F**	**G**

Hence, a p^2 configuration can give rise to D, P, and S terms; they differ in energy on account of the different electrostatic interactions between the electrons arising from their different orbital occupations.

A closed shell has zero orbital angular momentum because all the individual orbital angular momenta sum to zero. Therefore, when working out term symbols, we need to consider only the electrons of the unfilled shell. In the case of a single electron outside a closed shell, the value of L is the same as the value of l, and so the configurartion $[Ne]3s^1$ has only an S term.

Deriving the total angular momentum of a configuration

Let us find the terms that can arise from various configurations:

(a) d^2: We use the Clebsch-Gordan series and begin by finding the minimum value of L (so that we know where the series terminates). Minimum value: $|l_1 - l_2| = |2 - 2| = 0$. Therefore,

$$L = 2 + 2, 2 + 2 - 1, ..., 0 = 4, 3, 2, 1, 0$$

corresponding to G, F, D, P, S terms, respectively.

(b) p^3: In the case of three electrons, we use two series in succession: first we couple two electrons, and then we couple the third to each combined state. First coupling: Minimum value: $|1 - 1| = 0$. Therefore,

$$L' = 1 + 1, 1 + 1 - 1, ..., 0 = 2, 1, 0$$

Now couple l_3 with $L' = 2$, to give $L = 3, 2, 1$

with $L' = 1$, to give $L = 2, 1, 0$

with $L' = 0$, to give $L = 1$

The overall result is $L = 3, 2, 2, 1, 1, 1, 0$

giving one F, two D, three P, and one S terms.

(c) f^1d^1: Minimum value: $|l_1 - l_2| = |3 - 2| = 1$. Therefore,

$L = 3 + 2, 3 + 2 - 1, ..., 1 = 5, 4, 3, 2, 1$, corresponding to H, G, F, D, P terms.

(d) d^3: First coupling: Minimum value: $|2 - 2| = 0$. Therefore,

$$L' = 2 + 2, 2 + 2 - 1, ..., 0 = 4, 3, 2, 1, 0$$

Now couple l_3 with $L' = 4$, to give $L = 6, 5, 4, 3, 2$

with $L' = 3$, to give $L = 5, 4, 3, 2, 1$

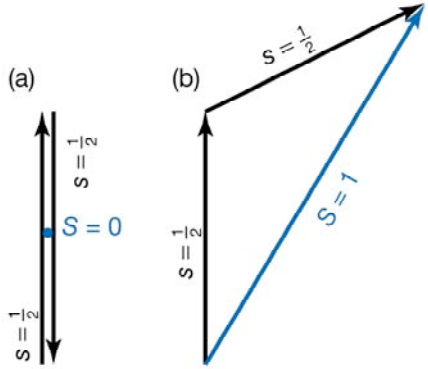
with $L' = 2$, to give $L = 4, 3, 2, 1, 0$

with $L' = 1$, to give $L = 3, 2, 1$

with $L' = 0$, to give $L = 2$

The overall result is $L = 6, 5, 5, 4, 4, 4, 3, 3, 3, 3, 2, 2, 2, 2, 2, 1, 1, 1, 0$

giving one I, two H, three G, four F, five D, three P, and one S terms.



The multiplicity

When there are several electrons to be taken into account, we must assess their **total spin angular momentum** S. Once again, we use the Clebsch-Gordan series to decide on the value of S, noting that each electron has $s = 1/2$, which gives $S = 1, 0$

If there are three electrons, the total spin angular momentum is obtained by coupling the third spin to each of the values of S for the first two spins:

$S = 3/2, 1/2$ and $S = 1/2$

The **multiplicity** of a term is the value of $2S + 1$. When $S = 0$ (as for a closed shell) the electrons are all paired and there is no net spin: this gives a singlet term, such as ^{1}S. A single electron has $S = s = 1/2$, and so a configuration such as [Ne]3s^1 can give rise to a doublet term, ^{2}S. The configuration [Ne]3p^1 likewise is a doublet, ^{2}P. When there are two unpaired electrons, $S = 1$ and so $2S + 1 = 3$, giving a triplet term, such as ^{3}D. We discussed the energies of singlets and triplets earlier and saw that their energies differ on account of the different effects of spin correlation.

The total angular momentum

As we have seen, the total angular momentum quantum number j tells us the relative orientation of the spin and orbital angular momenta of a single electron. The **total angular momentum** J does the same for several electrons. If there is a single electron outside a closed shell, then $J = j$, with j either $l + 1/2$ or $l - 1/2$. The [Ne]3s^1 configuration has $j = 1/2$ (because $l = 0$ and $s = 1/2$), and so the ^{2}S term has a single level, $^2S_{1/2}$. The [Ne]3p^1 configuration has $l = 1$, and $j = 3/2$ and $1/2$; the ^{2}P term therefore has two levels, $^2P_{3/2}$ and $^2P_{1/2}$, and these lie at different energies on account of the magnetic spin-orbit interaction.

If there are several electrons outside a closed shell we have to consider the coupling of all the spins and all the orbital angular momenta. This complicated problem can be simplified when the spin-orbit coupling is weak (for atoms of low atomic number) for then we can use the **Russell-Saunders coupling scheme**. The Russell-Saunders scheme is based on the view that if spin-orbit coupling is weak, then it is effective only when all the orbital angular momenta are operating cooperatively. We therefore imagine that all the orbital angular momenta of the electrons couple to give some total L, and that all the spins are similarly coupled to give some total S. Only at this stage we imagine the two kinds of momenta coupling through the spin-orbit interaction to give a total J. The permitted values of J are given by the Clebsch-Gordan series: $J = L+S, L+S-1, \ldots, |L-S|$

For example, in the case of the ^{3}D term of the configuration [Ne]$2p^1 3p^1$, the permitted values of J are 3, 2, 1 (because ^{3}D has $L = 2$ and $S = 1$), and so the term has three levels, $^3D_3$, $^3D_2$, and $^3D_1$.

When $L \geq S$, the multiplicity is equal to the number of levels, as in ^{2}P having the two levels $^2P_{3/2}$ and $^2P_{1/2}$ and ^{3}D the three levels, $^3D_3$, $^3D_2$, and $^3D_1$.

However, this is not the case when $L < S$: ^{2}S, for example, has only the single level $^2S_{1/2}$.

Deriving term symbols

Let us write the term symbols for the ground configurations of Na and F, and the excited configuration $1s^2 2s^2 2p^1 3p^1$ of C. The procedure is the following:

1) Write the configurations but ignore inner closed shells.

2) Couple the orbital momenta to find L and the spins to find S.

3) Couple L and S to find J. Express the term as $^{2S+1}\{L\}_J$, where $\{L\}$ is the appropriate letter (S, P, D, F, etc.).

For instance, for Na the configuration is [Ne]$3s^1$, and we consider the single 3s electron. Since $L = l = 0$ and $S = s = 1/2$, it is possible for $J = j = s = 1/2$ only. Hence, the term symbol is $^2S_{1/2}$.

For F, we can treat the single gap in $2p^6$ as a single particle. The configuration [He]$2s^2 2p^5$ can be then written as [Ne]$2p^{-1}$. Hence $L = l = 1$ and $S = s = 1/2$. Two values of $J = j$ are allowed: $J = 3/2, 1/2$. Hence the term symbols for the two levels are $^2P_{3/2}$, $^2P_{1/2}$.

For C, the configuration is effectively $2p^1 3p^1$. This is a two-electron problem, and $l_1 = l_2 = 1$, $s_1 = s_2 = 1/2$. It follows that $L = 2, 1, 0$ and $S = 1, 0$. The terms are therefore ^3D and ^1D, ^3P and ^1P, and ^3S and ^1S. For ^3D, $L = 2$ and $S = 1$; hence $J = 3, 2, 1$, and the levels are $^3D_3$, $^3D_2$, and $^3D_1$. For ^1D, $L = 2$ and $S = 0$, so that the single level is $^1D_2$. The triplet of levels of ^3P is $^3P_2$, $^3P_1$, and $^3P_0$, and the singlet is $^1P_1$. For the ^3S term there is only a single level, $^3S_1$ (because $J = 1$ only), and the singlet term is $^1S_0$.

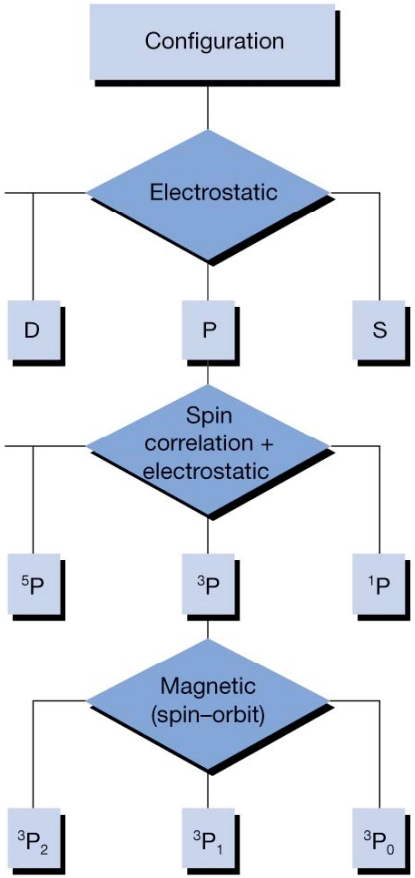
Relative energies of different terms

Once the terms are known, it is necessary to find their relative energies in order to choose which term characterizes the ground state of the atom. This can be done by a set of simple rules, called *Hund's rules*:

(a) The terms are ordered according to their S values, the term with maximum S being most stable and the stability decreasing with decreasing S. Thus, the ground state has *maximum spin multiplicity*.

(b) For a given value of S (given spin multiplicity), the state with *maximum* L is most stable.

(c) For given S and L, the *minimum* J value is most stable if there is a single open subshell that is *less than half-full* and the *maximum* J is most stable if the subshell is *more than half-full*.



Rules (a) and (b) arise from the electron-electron (electrostatic) interaction between the electrons, while rule (c) is a consequence of the spin-orbit (magnetic) interaction. Rule (a) is easy to understand, in that maximum S implies parallel spin (i.e., the same m_s quantum numbers for $M_S = S$). This means that the m quantum numbers must be different, corresponding to the fact that the electrons occupy different orbitals, which minimizes the repulsive interaction. The maximum L rule has a similar origin. The J rule derives from the relationship between the sign of the total orbital magnetic moment and the number of the electrons present in a subshell relative to the number that can be accommodated.

Russell-Saunders coupling fails when the spin-orbit-coupling is large (in heavy atoms). In that case, the individual spin and orbital momenta of the electrons are coupled into individual j values; then these momenta are combined into a grand total J. This is called ***jj*-coupling**. For example, in a p^2 configuration, the individual values of j are 3/2 and 1/2 for each electron. If the spin and the orbital angular momentum of each electron are coupled together strongly, it is best to consider each electron as a particle with angular momentum $j = 3/2$ or 1/2. These individual total momenta then couple as follows:

$j_1 = 3/2$ and $j_2 = 3/2$ - $J = 3, 2, 1, 0$; $j_1 = 3/2$ and $j_2 = 1/2$ - $J = 2, 1$

$j_1 = 1/2$ and $j_2 = 3/2$ - $J = 2, 1$ $\quad$ $j_1 = 1/2$ and $j_2 = 1/2$ - $J = 1, 0$

For heavy atoms ($Z \geq 40$), in which *jj*-coupling is appropriate, it is best to discuss their energies using these quantum numbers.

Selection rules

Any state of the atom, and any spectral transition, can be specified using term symb For example, the transition giving rise to the yellow sodium doublet are

$3p^1\ ^2P_{3/2} \rightarrow 3s^1\ ^2S_{1/2}$ and $3p^1\ ^2P_{1/2} \rightarrow 3s^1\ ^2S_{1/2}$

The configuration need not always be specified and a simpler specification of these transitions is

$^2P_{3/2} \rightarrow\ ^2S_{1/2}$ and $^2P_{1/2} \rightarrow\ ^2S_{1/2}$

Note that according to the accepted convention the upper term precedes the lower:

$^2P_{3/2} \leftarrow\ ^2S_{1/2}$ and $^2P_{1/2} \leftarrow\ ^2S_{1/2}$

We have seen that selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon has a spin of 1. They can therefore be expressed in terms of the term symbols, because the latter carry information about angular momentum. A detailed analysis leads to the following rules:

$$\Delta S = 0 \qquad \Delta L = 0, \pm 1 \qquad \text{with } \Delta l = \pm 1$$

$$\Delta J = 0, \pm 1 \quad \text{but} \quad J = 0 \quad \text{cannot combine with} \quad J = 0$$

The rule about ΔS (no change of overall spin) stems from the fact that the light does not affect the spin directly. The rule about ΔL and Δl expresses the fact that the orbital angular momentum of an individual electron must change (so $\Delta l = \pm 1$), but whether this results in an overall change of L depends on coupling.

These selection rules apply when Russell-Saunders coupling is valid (in light atoms). If we insist on labeling the terms of heavy atoms with symbols like ^3D, then we shall find that the selection rules progressively fail as the atomic number increases because the quantum numbers S and L become ill defined as jj-coupling becomes more appropriate. For this reason, transition between singlet and triplet states (for which $\Delta S = \pm 1$), while forbidden in light atoms, are allowed in heavy atoms.