6. Many-electron atoms

The helium atom

The Hamiltonian for He (with clamped nucleus) is

$$\begin{aligned} H_{\text{He}} = &-\frac{\hbar^2}{2m_e}\nabla_1^2 \\ &-\frac{\hbar^2}{2m_e}\nabla_2^2 \\ &-\frac{Ze^2}{4\pi\varepsilon_0 r_1} \\ &-\frac{Ze^2}{4\pi\varepsilon_0 r_2} \\ &+\frac{e^2}{4\pi\varepsilon_0 r_{12}} \end{aligned} \tag{1}$$

Because of the term in $1/r_{12}$this can't be separated into $H(1) + H(2)$, so the wavefunction can't be written as $\Psi = \psi(1)\psi(2)$.

6.1 Central field approximation

However we can write *approximately*

$$H_{\mathrm{He}} \approx H(1) + H(2) \qquad (2)$$

with

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r) \qquad (3)$$

where V includes a spherical average of the repulsion from the other electron.

This is the *central field approximation*, and it allows us to treat the electrons as if they move independently of each other.

That is, $\Psi = \psi(1)\psi(2)$, with $H\psi = E\psi$.

Writing out the kinetic energy term gives (in atomic units)

$$H = -\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{\mathbf{l}}^2}{2r^2} + V(r)$$

The important feature is that V still depends only on r, not on θ and φ.

Because of this we can still write

$$\psi_{nlm} = R_{nl}\left(r\right)Y_{lm}(\theta,\varphi)$$

where $Y_{lm}(\theta, \varphi)$ is a spherical harmonic, just as before, but $R_{nl}(r)$ now satisfies a different radial equation:

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial R_{nl}}{\partial r}+\frac{l\left(l+1\right)}{2r^2}R_{nl}+V\left(r\right)R_{nl}=E_{nl}R_{nl}$$

The Self-Consistent Field method

The radial equation is

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial R_{nl}}{\partial r}+\frac{l\left(l+1\right)}{2r^2}R_{nl}+V\left(r\right)R_{nl}=E_{nl}R_{nl}$$

V is an average of the interactions with the other electron (or electrons, in general), so we can't calculate it until we know where the electrons are. We have to start by guessing the form of the orbitals, and then

(i) use the orbitals to evaluate $V(r)$,

(ii) solve the eq. to get new orbitals,

and repeat the process until the new orbitals agree with the old ones

This is called the *Self-Consistent Field* or *SCF* method.

The potential acting on the electron is spherical

Each electron in an atom moves independently in a central potential due to the Coulomb attraction of the nucleus and the average effect of the other electrons in the atom.

Hartree’s procedure is as follows

$$\phi_0 = s_1(r_1,\theta_1,\phi_1)s_2(r_2,\theta_2,\phi_2)\cdots s_n(r_n,\theta_n,\phi_n) \qquad s_i = f(r)Y_m^l(\theta,\phi)$$

electron 1

$$\rho_2 = -e\,|s_2|^2 \qquad V_{12} = \frac{Q_1}{4\pi\varepsilon_0}\int\frac{\rho_2}{r_{12}}dv_2 = e'^2\int\frac{|s_2|^2}{r_{12}}dv_2$$

$$e' = \frac{e}{4\pi\varepsilon_0}$$

$$V_{12} + V_{13} + \cdots + V_{1n} = \sum_{j=2}^{n} e'^2\int\frac{|s_j|^2}{r_{ij}}dv_j$$

$$V_1(r_1,\theta_1,\phi_1) = \sum_{j=2}^{n} e'^2\int\frac{|s_j|^2}{r_{1j}}dr_j - \frac{Ze'^2}{r_1} = V_1(r_1)$$

$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 + V_1(r_1)\right]t_1(1) = \varepsilon_1 t(1)$$

Orbital energies in many-electron atoms

Because we now have a potential $V(r)$ instead of Z/r, the energies change, and they now depend on l as well as n. We can see why by comparing the radial functions for the $2s$ and $2p$ orbitals in hydrogen.

Remember that in the hydrogen atom, the $2s$ and $2p$ orbitals have the *same* energy. The potential energy contribution is

$$\begin{aligned}\langle V\rangle_{nl} &= \int \psi_{nlm}(\boldsymbol{r})^{*}\hat{V}(r)\psi_{nlm}(\boldsymbol{r})r^{2}\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi \\ &= \int (R_{nl}Y_{lm})^{*}\,\hat{V}(r)R_{nl}Y_{lm}r^{2}\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi \\ &= \int R_{nl}^{2}\hat{V}(r)r^{2}\mathrm{d}r = \int \hat{V}(r)P_{nl}(r)\mathrm{d}r\end{aligned}$$

When $\hat{V} = -1/r$ this is the same for both ψ_{2s} and ψ_{2p}.

For example

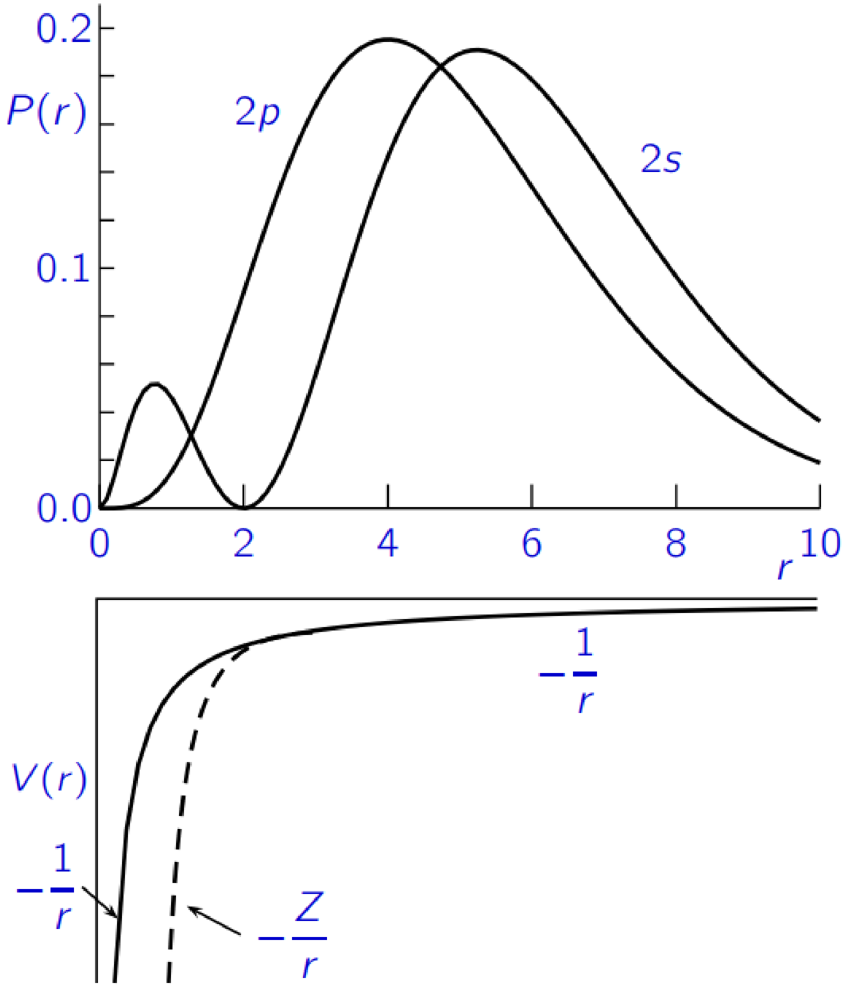
$$\langle V\rangle_{2p} = \int R_{2p}^{2}\hat{V}(r)r^{2}\mathrm{d}r = -\frac{1}{24}\int_{0}^{\infty} r^{3}\mathrm{e}^{-r}\mathrm{d}r = -3!/24 = -1/4$$

Radial probability densities in the H atom

Radial probability densities

$$P(r) = r^2 R_{nl}(r)^2$$

for 2*s* and 2*p* hydrogen atom orbitals.
Schematic potential energy curves for the hydrogen atom (solid line) and for a many-electron atom (dashed line).

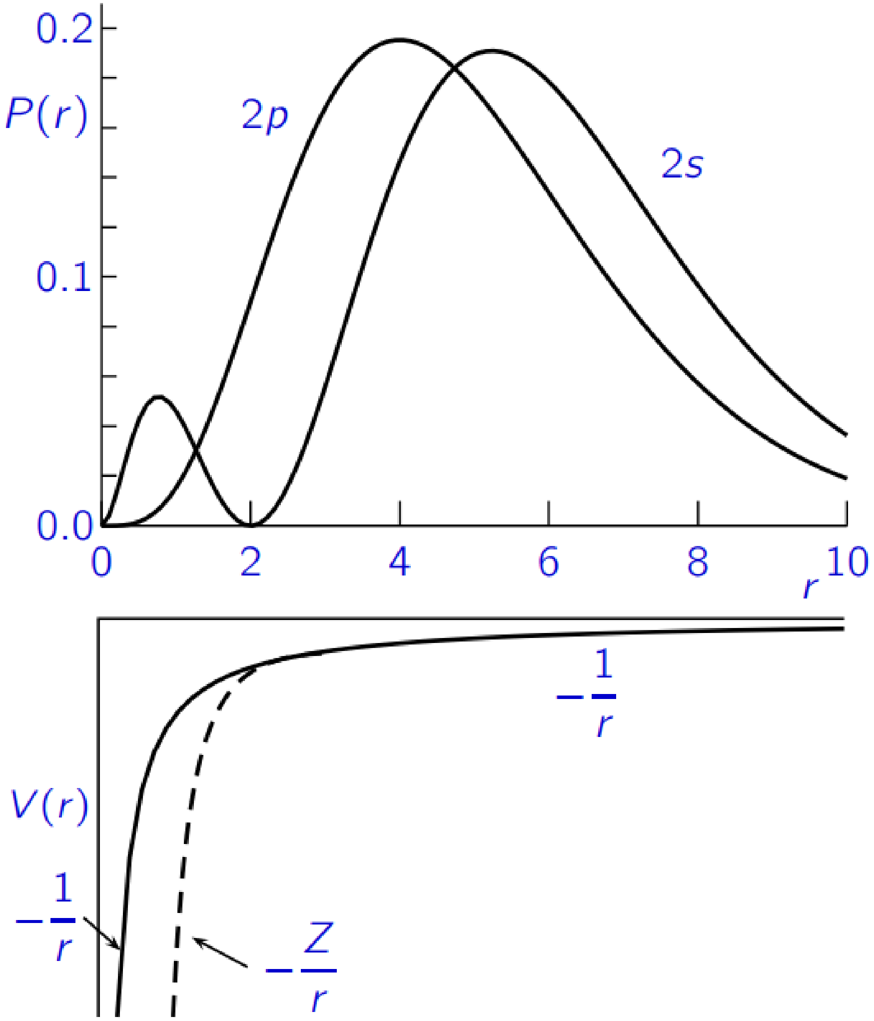


Orbital energies in many-electron atoms

For the many-electron atom, the operator $\hat{V} = -1/r$ is replaced by the function shown by the clashed line in the figure, which behaves like $-1/r$ for large r, but like $-Z/r$ near the nucleus.

The orbitals in a many-electron atom are not the same as in the hydrogen atom, but the $2s$ wave-function always has a radial node, and consequently a peak in the probability density near the nucleus, while the $2p$ *radial density* has no node.

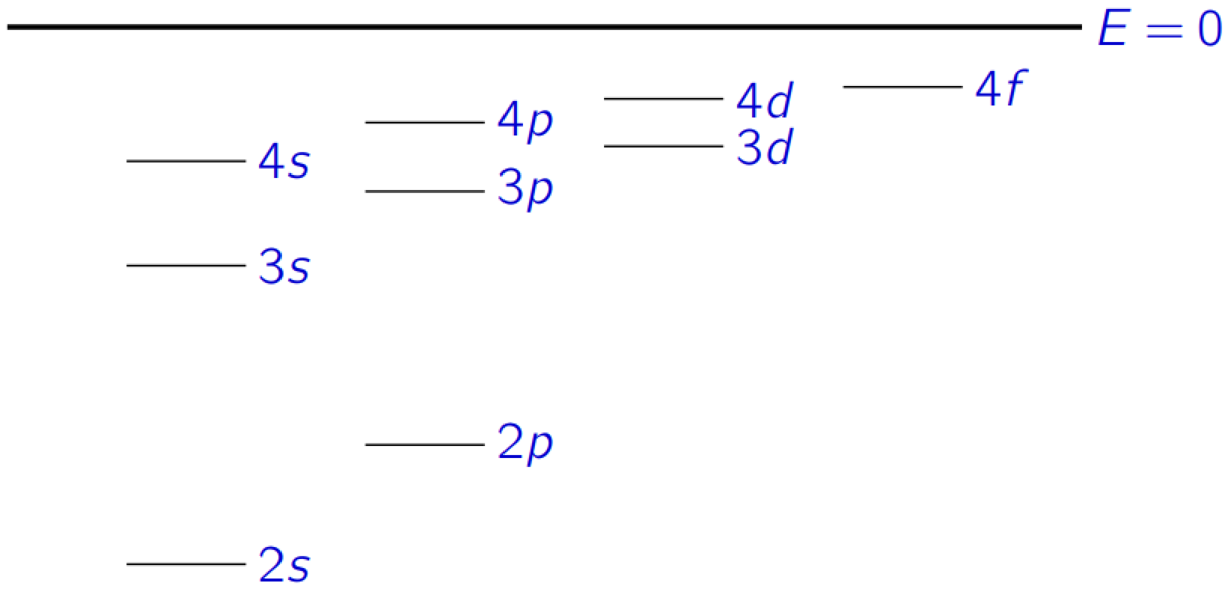
Consequently a $2s$ electron in a many-electron atom feels the attraction of the nucleus more strongly than a $2p$ electron does, so it has a lower energy.



A $2p$ electron is more effectively *screened* from the nucleus by the other electrons than a $2s$ electron, or equivalently the $2s$ electron *penetrates* through the other electrons to the nucleus more effectively than the $2p$.

Either way, the $2s$ orbitals have lower energy than the $2p$, and the difference in energy increases as we go across the period from Li to Ne.

The same thing happens in each row of the periodic table, so the orbital energy level pattern becomes something like the following (omitting the $1s$ level):



In the hydrogen-like atom the orbital energies are $-Z^2/2n^2$. In many-electron atoms, the nuclear charge is screened by the other electrons and the energy does not increase in magnitude so quickly with increasing Z. However it does increase, so the electrons with given principal quantum number become more strongly bound as Z increases. The orbital energies can be expressed very roughly as $-Z_{\mathrm{eff}}{}^2/2n^2$, where Z_{eff} depends on both n and l, and is given by *Slater's rules:*

$Z_{\mathrm{eff}} = Z - s_{nl}$, where for electrons with principal quantum number $n > 1$,

$$s_{nl} = 0.35(N_n - 1) + 0.85 N_{n-1} + N_{\mathrm{core}}$$

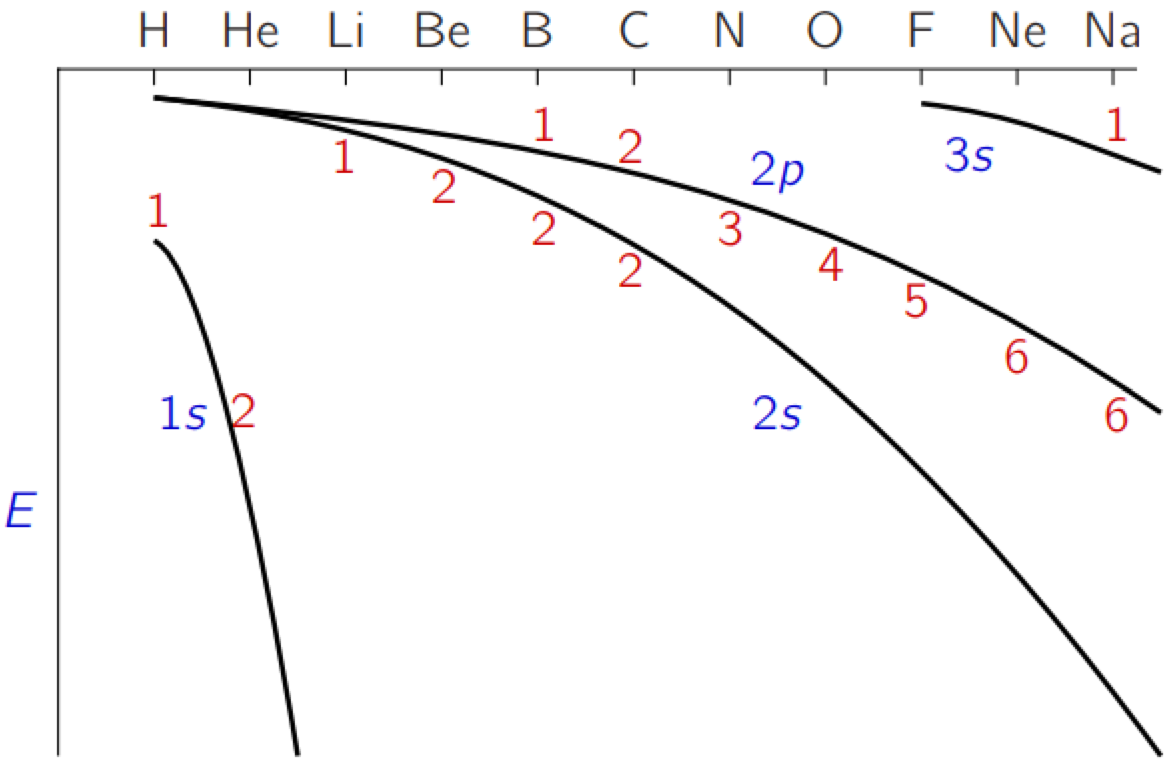
Here N_n is the number of electrons with principal quantum number n, and N_{core} is the number with principal quantum number less than $n - 1$.

$s_{1s} = 0.3$ is a special case.

The energy difference between 2s and 2p increases quite sharply:

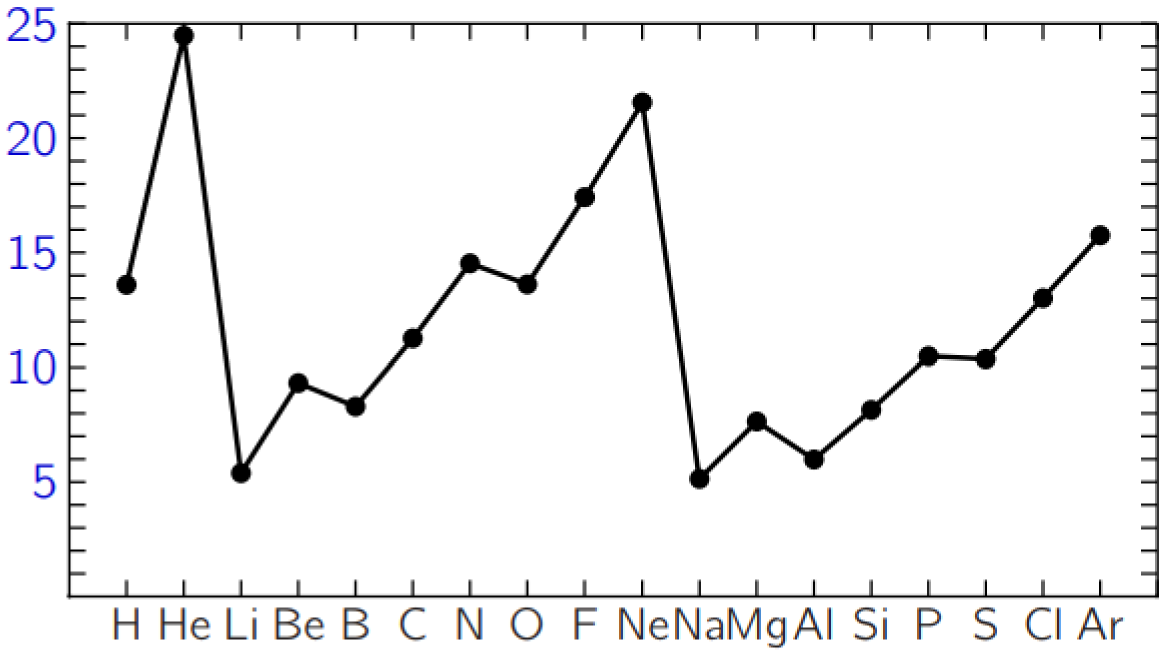
$$E_{2p} - E_{2s} : 0.07 E_h = 180 \text{ kJ mol}^{-1} \text{ for Li}$$

$$0.77 E_h = 2000 \text{ kJ mol}^{-1} \text{ for F}$$



Ionization energies

The *ionization energy* is the energy needed to remove one electron from the atom, to form the positive ion. Because of the general downward tend in orbital energies, the ionization energy increases across a period, but the trend is interrupted where the electrons begin to fill a new shell, for instance between Be and B and between Ne and Na. The steps between N and O and between P and S are less easily explained, and we shall return to that later.



Atomic ionization energies (*e*V).

Zeeman Effect

The splitting of a spectral line into two or more components of slightly different frequency when the light source is placed in a magnetic field. It was first observed in 1896 by the Dutch physicist Pieter Zeeman as a broadening of the yellow D-lines of sodium in a flame held between strong magnetic poles.

The (normal) Zeeman effect can be understood classically, as Lorentz predicted, as the interaction energy of an orbiting electron with the magnetic field.

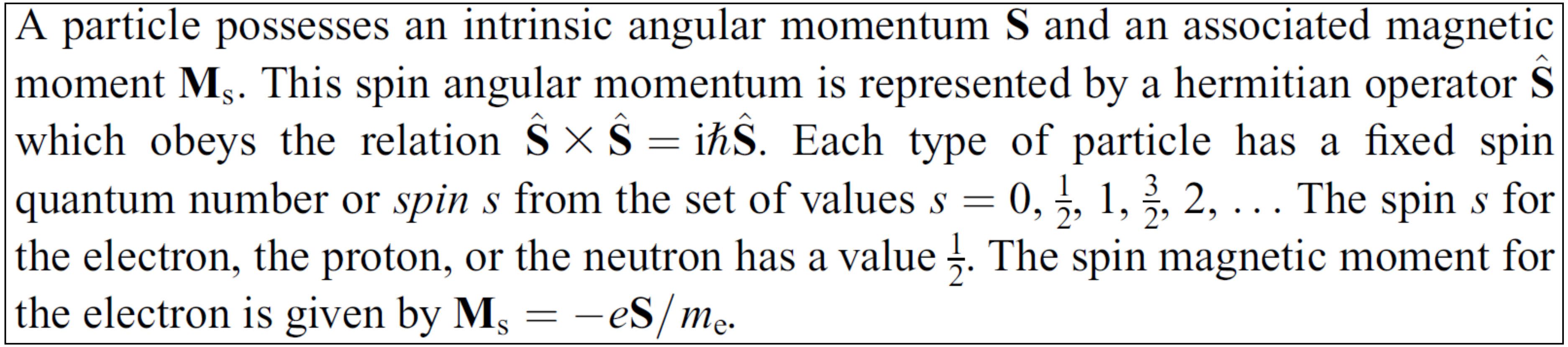
This "anomalous" Zeeman effect was eventually explained by the quantum mechanical effects of spin.

Spin

One of the more mysterious features of quantum mechanics is the property called *spin*, which has no classical analogue. It does have the properties of an angular momentum, as the name implies, but it should not be thought of in classical terms.

We have seen that an electron in an atom has orbital angular momentum, usually designated by the symbol $\hat{\boldsymbol{l}}$, with quantum numbers l describing the magnitude $\hbar\sqrt{l(l+1)}$ of the angular momentum vector, and m_l describing its z component. Both of these quantum numbers have to be integers because of the boundary conditions on the wavefunction.

An electron also has an intrinsic angular momentum called spin, designated by the symbol $\hat{\boldsymbol{s}}$. It has quantum numbers s and m_s, describing its magnitude and z component.



A particle possesses an intrinsic angular momentum **S** and an associated magnetic moment $\mathbf{M}_\mathrm{s}$. This spin angular momentum is represented by a hermitian operator $\hat{\mathbf{S}}$ which obeys the relation $\hat{\mathbf{S}} \times \hat{\mathbf{S}} = i\hbar\hat{\mathbf{S}}$. Each type of particle has a fixed spin quantum number or *spin* s from the set of values $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ The spin s for the electron, the proton, or the neutron has a value $\frac{1}{2}$. The spin magnetic moment for the electron is given by $\mathbf{M}_\mathrm{s} = -e\mathbf{S}/m_\mathrm{e}$.

Spin is not described by angular coordinates in the same way as orbital angular momentum, and the quantum numbers are not restricted by boundary conditions. It turns out that they may have half-odd-integer values in addition to the integer values.

$$\hat{S} = \mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z$$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

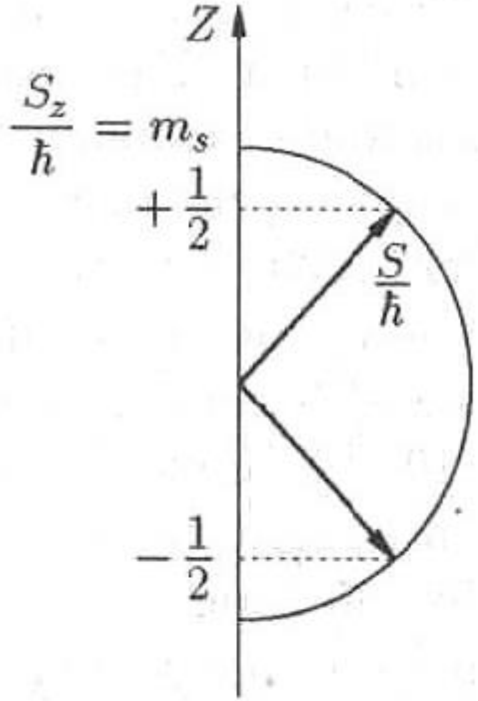
$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z \qquad \left[\hat{S}^2, \hat{S}_x\right] = \left[\hat{S}^2, \hat{S}_y\right] = \left[\hat{S}^2, \hat{S}_z\right] = 0$$

The differences between spin and orbital angular momentum are:

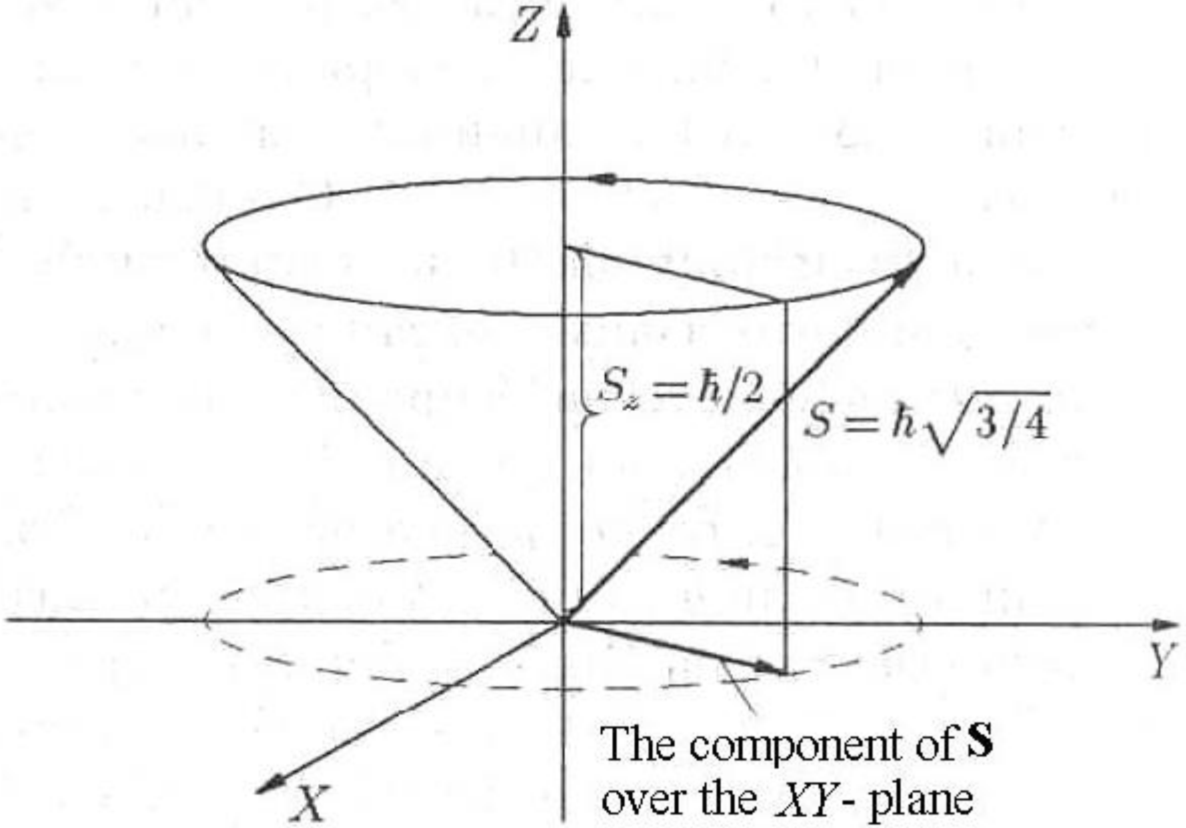
- The spin quantum numbers need not be integers ——they may be half-odd-integer.
- The quantum number s has a fixed value for a particular kind of fundamental particle. It is always $\frac{1}{2}$ for electrons (and for protons and neutrons).

We note in passing that nuclei also have spin (important in n.m.r.). The nuclear spin operator is usually designated I, with quantum numbers I and m_I. Some values are:

H (proton)	$\boldsymbol{I} = \frac{1}{2}$
D (deuteron)	$\boldsymbol{I} = 1$
F	$\boldsymbol{I} = \frac{1}{2}$
^{16}O, ^{12}C	$\boldsymbol{I} = 0$
^{13}C	$\boldsymbol{I} = \frac{1}{2}$



$$S = \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$$



The component of **S** over the *XY*- plane

Orbital angular momentum

$\hat{\mathbf{L}}\,(\hat{L}_x, \hat{L}_y, \hat{L}_z),$

$L = \hbar\sqrt{l(l+1)},$

$l = 0,\ 1,\ 2,\ \ldots,$

$L_z = m\hbar,$

m- magnetic number,

$m = 0,\ \ \pm 1,\ \ \pm 2, \ldots,$

$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2,$

$[\hat{L}^2 \hat{L}_{x_j}] = 0,\ \ x_j = x,\ y,\ \mathrm{z},$

$[\hat{L}_x \hat{L}_y] = i\hbar\hat{L}_z,$

$[\hat{L}_z \hat{L}_x] = i\hbar\hat{L}_y,$

$[\hat{L}_y \hat{L}_z] = i\hbar\hat{L}_x,$

Spin angular momentum

$\hat{\mathbf{S}}\,(\hat{S}_x, \hat{S}_y, \hat{S}_z),$

$S = \hbar\sqrt{s(s+1)},$

$s = 1/2,$

$S_z = m_s\hbar,$

m_s - magnetic spin number

$m_s = \pm 1/2$

$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,$

$[\hat{S}^2 \hat{S}_{x_j}] = 0,\ \ x_j = x,\ y,\ \mathrm{z},$

$[\hat{S}_x \hat{S}_y] = i\hbar\hat{S}_z,$

$[\hat{S}_z \hat{S}_x] = i\hbar\hat{S}_y,$

$[\hat{S}_y \hat{S}_z] = i\hbar\hat{S}_x.$

Notations for spin

The m_s quantum number follows the usual rules for angular momentum: it can take values between s and $-s$ in integer steps. Since $s = \frac{1}{2}$ for an electron, m_s can take only the values $\frac{1}{2}$ or $-\frac{1}{2}$.

The state with $m_s = \frac{1}{2}$ ('spin up') is denoted by the symbol α, and the state with $m_s = -\frac{1}{2}$ ('spin down') by the symbol β These can be thought of as wavefunctions, but there is no coordinate in the conventional sense. We can also use σ_{m_s} for a generic spin function; i.e., $\sigma_{1/2} = \alpha$ and $\sigma_{-1/2} = \beta$.

$$\hat{s}_z\alpha = \frac{1}{2}\hbar\alpha \qquad \hat{s}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha$$

$$\hat{s}_z\beta = -\frac{1}{2}\hbar\beta \qquad \hat{s}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta = \frac{3}{4}\hbar^2\beta$$

The symbols ↿ and ⇂ are commonly used in orbital energy level diagrams to denote electron occupancy with spin up and down respectively.

Wavefunctions including spin

The spin is a new degree of freedom, so we can construct a complete wavefunction for the hydrogen atom by multiplying together an atomic orbital and a spin function. A general one-electron atomic wavefunction or *spin-orbital* is then

$$|nlm_l m_s\rangle = R_{nl}(r)\,Y_{l,m_l}(\theta,\varphi)\,\sigma_{m_s}$$

and it satisfies the eigenvalue equations

$$H\,|nlm_l m_s\rangle = E_{nl}\,|nlm_l m_s\rangle$$

$$\hat{\boldsymbol{l}}^2\,|nlm_l m_s\rangle = l(l+1)\hbar^2\,|nlm_l m_s\rangle$$

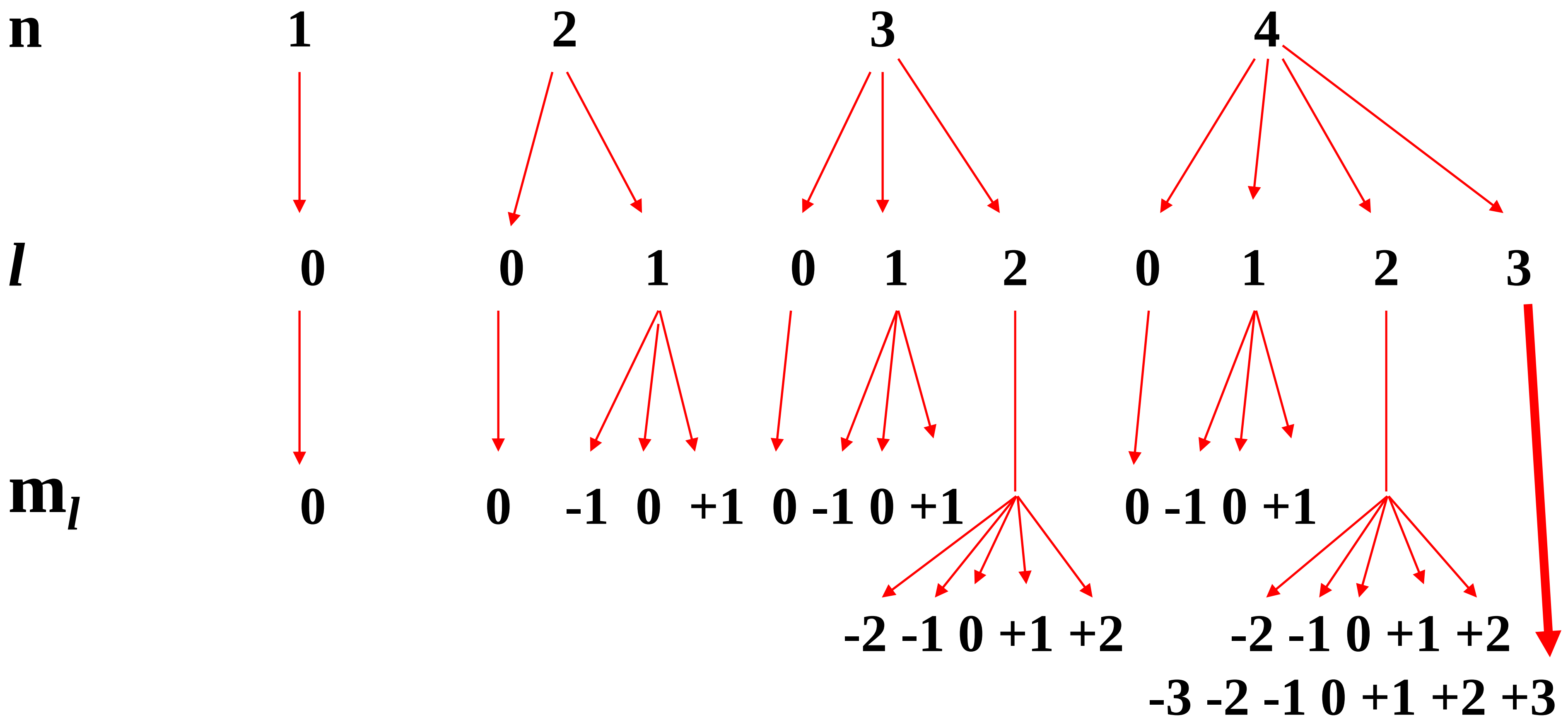
$$\hat{l}_z\,|nlm_l m_s\rangle = m_l\hbar\,|nlm_l m_s\rangle$$

$$\hat{\boldsymbol{s}}^2\,|nlm_l m_s\rangle = s(s+1)\hbar^2\,|nlm_l m_s\rangle, \text{with } s = \frac{1}{2}$$

$$\hat{s}_z\,|nlm_l m_s\rangle = m_s\hbar\,|nlm_l m_s\rangle$$

We don't need to list the quantum number s because it is always $\frac{1}{2}$.

Quantum Numbers



n **1** **2** **3** **4**

l **0** **0 1** **0 1 2** **0 1 2 3**

m_l **0** **0** **-1 0 +1** **0** **-1 0 +1** **0 -1 0 +1**

-2 -1 0 +1 +2 **-2 -1 0 +1 +2**

-3 -2 -1 0 +1 +2 +3

- The total number of orbitals for a given value of n is n^2. Considering the spin, the degeneracy is $2\ n^2$

Two spins

If we have two electrons, they each have spin $\frac{1}{2}$ and each has spin states α and β. Using subscripts 1 and 2 to label the electrons, the possible states of the system are

$$\alpha_1\alpha_2,\ \alpha_1\beta_2,\ \beta_1\alpha_2 \text{ or } \beta_1\beta_2$$

Now the z component of the total spin is described by the operator $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$, which is just the sum of the z components of the individual spin vectors.
$\hat{s}_{1z}$ doesn't have any effect on the spin functions of electron 2, and vice versa, so

$$\begin{aligned}\hat{S}_z\alpha_1\alpha_2 &= \left(\hat{s}_{1z} + \hat{s}_{2z}\right)\alpha_1\alpha_2 \\ &= \left(\frac{1}{2}\hbar\alpha_1\right)\alpha_2 + \alpha_1\left(\frac{1}{2}\hbar\alpha_2\right) = \hbar\alpha_1\alpha_2\end{aligned}$$

and $\alpha_1\alpha_2$ is an eigenfunction of S_z with eigenvalue $\hbar$, which we can write as $M_s\hbar$ with $M_s = 1$.

Two spins: singlet and triplet states

Thus $M_s = 1$ for the wavefunction $\alpha_1\alpha_2$. In the same way, $\alpha_1\beta_2$ and $\beta_1\alpha_2$ have $M_s = 0$, and $\beta_1\beta_2$ has $M_s = -1$.

Remembering that angular momentum eigenfunctions come in sets with $M = J, J-1, \dots, -J$, we see that we have a set with $M_s = 1, 0\ and - 1$, which has $S = 1$, and a second function with $M_s = 0$ which is the sole member of a set with $S = 0$.

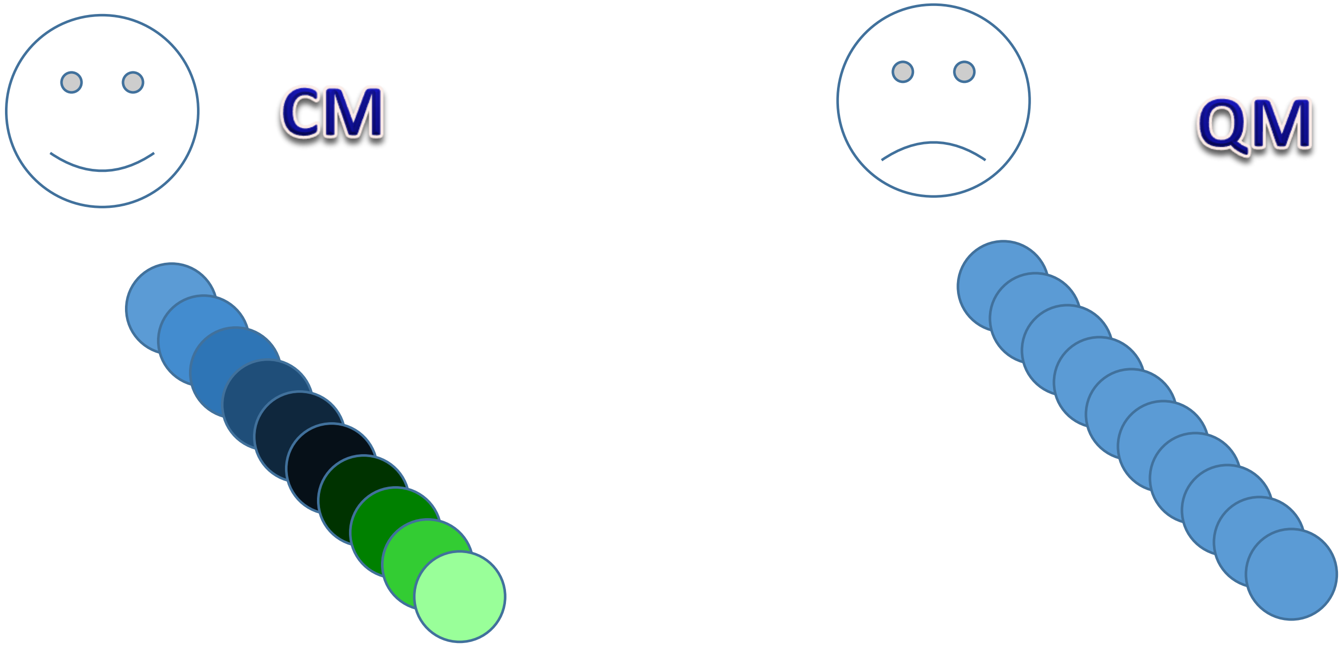
Clearly $\alpha_1\alpha_2$ and $\beta_1\beta_2$ belong to the set of functions with $S = 1$.

$\alpha_1\alpha_2$	$M_s = 1$
$\alpha_1\beta_2$,$\beta_1\alpha_2$	0
$\beta_1\beta_2$	-1

M_s	$S = 1$ (triplet)	$S = 0$ (singlet)
1	$\alpha_1\alpha_2$	
0	$\sqrt{\frac{1}{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$	$\sqrt{\frac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$
-1	$\beta_1\beta_2$	

The third function of this set turns out to be neither $\alpha_1\beta_2$ nor $\beta_1\alpha_2$ but a mixture, $\sqrt{\frac{1}{2}}(\alpha_1\beta_2 +$

Identical particles



Uncertainty Principle

All electrons are identical and therefore indistinguishable.

$$\hat{p}_{ij}\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n)=\psi(q_1,\cdots,q_j,\cdots q_i,\cdots q_n)$$

The permute operation should not change the physical property of the state wave function

$$\left|\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n)\right|^2 \propto \left|\psi(q_1,\cdots,q_j,\cdots q_i,\cdots q_n)\right|^2$$

$$\psi(q_1,\cdots,q_j,\cdots q_i,\cdots q_n) \ = c\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n)$$

$$\hat{p}_{ij}\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n) \ = c\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n)$$

$$c=\pm 1$$

$\psi(q_1,\cdots,q_i,\cdots q_j,\cdots q_n)$ the eigenfunctions of P_{ij}

symmetric or antisymmetric

$$\left[\hat{H},\hat{p}_{ij}\right]=0$$

The Pauli principle

In a two-electron atom, we might expect to be able to write down a wavefunction as a simple product of one-electron functions, such as

$$\Psi(1,2) = \psi_{1s}^{\alpha}(1)\psi_{2p_z}^{\beta}(2)$$

where 1 and 2 are abbreviations for all the coordinates of electrons 1 and 2 respectively, and $\psi_{1s}^{\alpha}(1)$ means $\psi_{1s}(\boldsymbol{r}_1)\ \alpha_1$.

However electrons are indistinguishable, so the probability density must be unafFected by exchanging the electrons. That is, we require

$$|\Psi(1,2)|^2 = |\Psi(2,1)|^2$$

or

$$\Psi(1,2) = \pm\Psi(2,1)$$

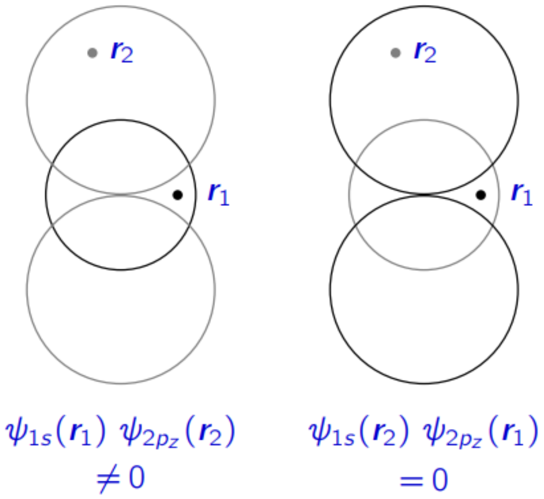
It has been found empirically that for electrons the minus sign always applies; that is, electronic wavefunctions are always *antisymmetric* with respect to exchange of electrons. This is the *Pauli principle.*

Exchange of electrons

Suppose we have an electron in a $1s$ orbital, and another in a $2p_z$ orbital. We ignore spin for the moment. Suppose also that we can attach labels to the electrons. If electron 1 is in the $1s$ orbital and electron 2 in the $2p$ orbital, the wavefunction would be $\psi_{1s}(\boldsymbol{r}_1)\ \psi_{2p_z}(\boldsymbol{r}_2)$. With the electrons at the positions shown, this wavefunction is nonzero.

If now we switch the electron labels in the wavefunction, so that electron 1 belongs to the $2p$ orbital and electron 2 to the $1s$ orbital, the wavefunction becomes $\psi_{1s}(\boldsymbol{r}_2)\ \psi_{2p_z}(\boldsymbol{r}_1)$. Electron 1 is at a node in the $2p$ orbital, so the wavefunction is now zero.

This example is evidently rather contrived, but it should be clear that in general a wavefunction $\psi_a(1)\ \psi_b(2)$ describing electron 1 in orbital ψ_a and electron 2 in orbital ψ_b will change if we switch the electron labels.



$\psi_{1s}(\boldsymbol{r}_1)\ \psi_{2p_z}(\boldsymbol{r}_2) \neq 0$

$\psi_{1s}(\boldsymbol{r}_2)\ \psi_{2p_z}(\boldsymbol{r}_1) = 0$

Symmetric and antisymmetric functions

Suppose that we add our two functions together:

$$\Psi_+(1,2) = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)$$

This new function doesn't change if we switch the electrons — it is *symmetric* with respect to electron exchange.

Alternatively we can subtract them:

$$\Psi_-(1,2) = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)$$

This function changes sign if we switch the electrons ——it is *antisymmetric* with respect to electron exchange.

One way to achieve antisymmetry for two electrons is to construct a symmetric orbital wave function and multiply it by an antisymmetric spin function, i.e., a singlet function. The other way is to use an antisymmetric orbital function and a symmetric spin function.

The Pauli principle

If we have two electrons in orbitals ψ_a and ψ_b ,the symmetric and antisymmetric orbital functions are

$$\Psi_+ = \sqrt{\frac{1}{2}}\left(\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)\right)$$

$$\Psi_- = \sqrt{\frac{1}{2}}\left(\psi_a(1)\psi_b(2)-\psi_a(2)\psi_b(1)\right)$$

We can combine these with singlet and triplet spin functions respectively to obtain acceptable overall wavefunctions.

$$\Psi_{\text{singlet}} = \sqrt{\frac{1}{2}}\left(\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)\right)\times\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2-\beta_1\alpha_2\right)$$

$$\Psi_{\text{triplet}} = \sqrt{\frac{1}{2}}\left(\psi_a(1)\psi_b(2)-\psi_a(2)\psi_b(1)\right)\times\begin{cases}\alpha_1\alpha_2\\ \sqrt{\frac{1}{2}}\left(\alpha_1\beta_2+\beta_1\alpha_2\right)\\ \beta_1\beta_2\end{cases}$$

Note that *if* $\psi_a = \psi_b$,the antisymmetric wavefunction Ψ_- vanishes. Thus two electrons can go into the same orbital only if they have opposite spins (singlet state).

N-particle systems

$$\hat{P}_{\alpha\beta}\Psi(i,\cdots,\underset{\alpha}{j},\cdots,\underset{\beta}{k},\cdots,l)=\Psi(i,\cdots,\underset{\alpha}{k},\cdots,\underset{\beta}{j},\cdots,l)$$

$$\boxed{\left[\hat{P}_{\alpha\beta},\hat{H}\right]=0,\qquad \alpha\neq\beta=1,2,\cdots,N}$$

They ($\hat{P}_{\alpha\beta}$ and $\hat{H}$) possess simultaneous eigenfunctions. There are only two functions, Ψ_S and Ψ_A, which are simultaneous eigenfunctions of $\hat{H}$ and all of the pairwise exchange operators $\hat{P}_{\alpha\beta}$

$$\hat{P}_{\alpha\beta}\Psi_S=\Psi_S,\qquad \alpha\neq\beta=1,2,\cdots,N$$

$$\hat{P}_{\alpha\beta}\Psi_A=-\Psi_A,\qquad \alpha\neq\beta=1,2,\cdots,N$$

How many operators $\hat{P}_{\alpha\beta}$ in N particle systems?

The operator $\hat{P}$ is any one of the $N!$ operators, including the identity operator, that permute a given order of particles to another order. The summation is taken over all $N!$ permutation operators. δ_P = 1 for sym; δ_P = -1 for anti-sym

$$\Psi_{S,A}=\left(N!\right)^{-1/2}\sum_{P}\delta_P\hat{P}\Psi(1,2,\cdots,N)$$

How to construct antisymmetric wave function?

For He atom:

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

For Li atom:

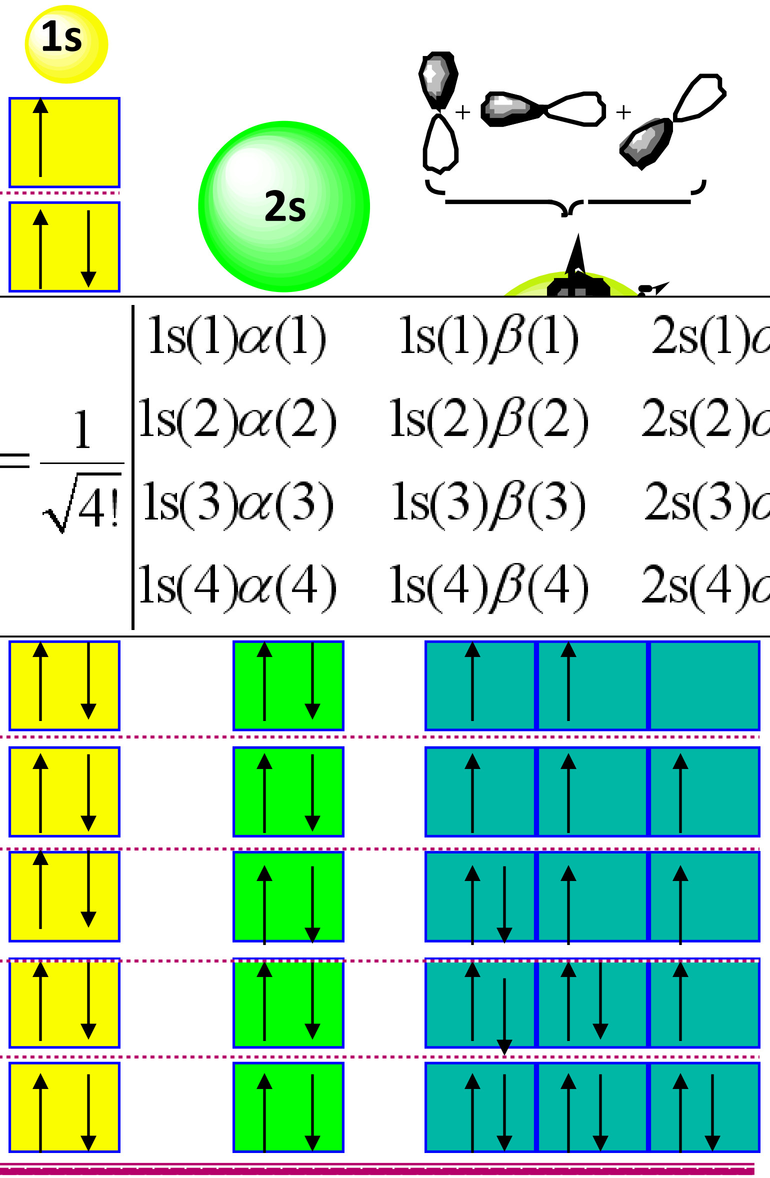
$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

Spin-orbital

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

The electronic configuration (for ground state)

- H = $1s^1$
- He = $1s^2$
- Li = $1s^2 2s^1$
- Be = $1s^2 2s^2$
- B = $1s^2 2s^2 2p^1$
- C = $1s^2 2s^2 2p^2$
- N = $1s^2 2s^2 2p^3$
- O = $1s^2 2s^2 2p^4$
- F = $1s^2 2s^2 2p^5$
- Ne = $1s^2 2s^2 2p^6$



$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

For a system of two identical particles

If a system is composed of several kinds of particles, then its wave function must be separately symmetric or antisymmetric with respect to each type of particle.

two bosons $$\Psi_{ab,S}(1,\,2) = 2^{-1/2}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

two fermions $$\Psi_{ab,A}(1,\,2) = 2^{-1/2}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

If states ψ_a and ψ_b are the same state ($a = b$)

$$\Psi_{aa,S}(1,\,2) = \psi_a(1)\psi_a(2)$$

$$\Psi_{aa,A}(1,\,2) = 0$$

Probability densities

$$\begin{array}{l} |\Psi_S|^2 = \\[1em] |\Psi_A|^2 = \end{array} \boxed{\begin{array}{l} \frac{1}{2}|\psi_a(1)|^2|\psi_b(2)|^2 + \frac{1}{2}|\psi_a(2)|^2|\psi_b(1)|^2 \\[1em] \frac{1}{2}|\psi_a(1)|^2|\psi_b(2)|^2 + \frac{1}{2}|\psi_a(2)|^2|\psi_b(1)|^2 \end{array}} \begin{array}{c} + \\[1em] - \end{array} \boxed{\begin{array}{l} \mathrm{Re}[\psi_a^*(1)\psi_b^*(2)\psi_a(2)\psi_b(1)] \\[1em] \mathrm{Re}[\psi_a^*(1)\psi_b^*(2)\psi_a(2)\psi_b(1)] \end{array}}$$

The probability density for one distinguishable particle

exchange density (indistinguishable)

when the two particles have the same coordinate value

$q_1 = q_2 = q_0$

$$\begin{aligned}
|\Psi_S|_0^2 &= \tfrac{1}{2}|\psi_a(\mathbf{q}_0)|^2|\psi_b(\mathbf{q}_0)|^2 + \tfrac{1}{2}|\psi_a(\mathbf{q}_0)|^2|\psi_b(\mathbf{q}_0)|^2 \\
&\quad + \mathrm{Re}[\psi_a^*(\mathbf{q}_0)\psi_b^*(\mathbf{q}_0)\psi_a(\mathbf{q}_0 0\psi_b(\mathbf{q}_0)] \\
&= 2|\psi_a(\mathbf{q}_0)|^2|\psi_b(\mathbf{q}_0)|^2 \\
|\Psi_A|_0^2 &= \tfrac{1}{2}|\psi_a(\mathbf{q}_0)|^2|\psi_b(\mathbf{q}_0)|^2 + \tfrac{1}{2}|\psi_a(\mathbf{q}_0)|^2|\psi_b(\mathbf{q}_0)|^2 \\
&\quad - \mathrm{Re}[\psi_a^*(\mathbf{q}_0)\psi_b^*(\mathbf{q}_0)\psi_a(\mathbf{q}_0)\psi_b(\mathbf{q}_0)] \\
&= 0
\end{aligned}$$

The two bosons have an increased probability density of being at the same point in space, while the two fermions have a vanishing probability density of being at the same point.

The exchange density is important only when the single-particle wave functions overlap substantially.

$$\psi_a^*(1)\psi_b(1)$$

$$\psi_b^*(2)\psi_a(2)$$

are then negligibly small and the exchange density essentially vanishes.

This expression is just the probability density for particle 1 confined to region A and particle 2 confined to region B. The two particles become distinguishable by means of their locations and their joint wave function does not need to be made symmetric or antisymmetric.

Fermi holes

Consider a wavefunction for two electrons, which we write in the form $\Psi(r_1, r_2)\sigma(1,2)$. r_1 and r_2 are the electron positions, and $\sigma(1,2)$ is a two-electron spin function, either singlet or triplet.

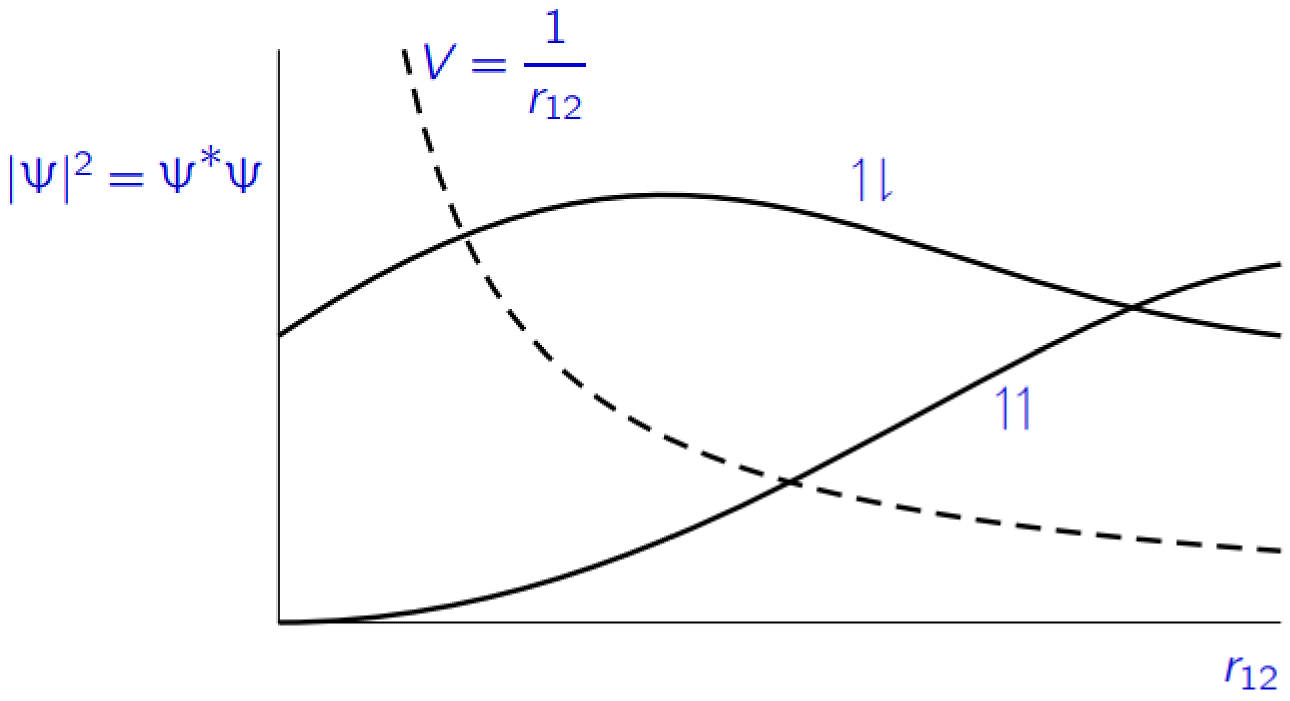
Because of the Pauli principle, the overall wavefunction must be antisymmetric:
$\Psi(r_1, r_2)\sigma(1,2) = -\Psi(r_2, r_1)\sigma(2,1)$.

Now if the two electrons are in the same place, then $r_1 = r_2 = r$, and the antisymmetry condition becomes $\Psi(r, r)\sigma(1,2) = -\Psi(r, r)\sigma(2,1)$.

If the spin function is symmetric (triplet), then $\sigma(1,2) = \sigma(2,1)$, and we find $\Psi(r, r) = -\Psi(r, r)$, so the wavefunction must vanish. That is, the probability of two electrons with the same spin being in the same place is *zero.*
There is no such limitation for electrons of opposite spin.

The probability density is a continuous function of the electronic coordinates, so there is a region around any electron where the probability of finding any other electron with the same spin is small. This region is called the *Fermi hole.*

Because the repulsion between two electrons is inversely proportional to the distance between them, the repulsion energy is substantially less for two electrons of the same spin than for two electrons of opposite spin



The helium atom

The $1s^2$ configuration of the He atom has only one possible state, a singlet, so we consider the excited ls2*s* configuration to explore the energy differences between singlet and triplet.

For the ls2*s* configuration, the possible states are the spin singlet, for which the orbital function is symmetric:

$$\Psi_+ = \sqrt{\frac{1}{2}}\left(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)\right)$$

and the spin triplet, for which the orbital function is antisymmetric:

$$\Psi_- = \sqrt{\frac{1}{2}}\left(\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)\right)$$

We need to find the expectation value of the electron repulsion:

$$\left\langle \frac{1}{r_{12}} \right\rangle_+ = \left\langle \Psi_+\sigma_{\text{singlet}} \left| \frac{1}{r_{12}} \right| \Psi_+\sigma_{\text{singlet}} \right\rangle = \left\langle \Psi_+ \left| \frac{1}{r_{12}} \right| \Psi_+ \right\rangle \left\langle \sigma_{\text{singlet}} \middle| \sigma_{\text{singlet}} \right\rangle = \left\langle \Psi_+ \left| \frac{1}{r_{12}} \right| \Psi_+ \right\rangle$$

The electron repulsion energy for the singlet state is:

$$
\begin{aligned}
E_{+}^{\mathrm{er}} &= \left\langle \Psi_{+} \middle| \frac{1}{r_{12}} \middle| \Psi_{+} \right\rangle \\
&= \iint \sqrt{\frac{1}{2}} \left(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1) \right) \times \frac{1}{r_{12}} \sqrt{\frac{1}{2}} \left(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1) \right) \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \\
&= J + K
\end{aligned}
$$

$$J = \iint \psi_{1s}(1)\psi_{2s}(2) \frac{1}{r_{12}} \psi_{1s}(1)\psi_{2s}(2) \mathrm{d}^3 r_1 \mathrm{d}^3 r_2$$

$$K = \iint \psi_{1s}(1)\psi_{2s}(2) \frac{1}{r_{12}} \psi_{1s}(2)\psi_{2s}(1) \mathrm{d}^3 r_1 \mathrm{d}^3 r_2$$

Coulomb and exchange integrals

Similarly, for the triplet state,

$$E_{-}^{\mathrm{er}} = \left\langle \Psi_{-} \left| \frac{1}{r_{12}} \right| \Psi_{-} \right\rangle = J - K$$

J is the *Coulomb integral*; it describes the repulsion between the charge densities $|\psi_{1s}|^2$ and $|\psi_{2s}|^2$, and is classical in nature. K is called an *exchange integral*, and cannot be understood in classical terms, except as the electrostatic energy of the 'overlap density' $\psi_{1s}\psi_{2s}$ with itself. It is always positive.

We see that the triplet state has a lower energy than the singlet.

Electron repulsion energies are large; two electrons at a distance of 1 bohr have a repulsion energy of 1 Hartree = 27.2 eV = 2626.5 kJ mol^{-1}. The separation between the singlet and triplet states in He l*s*2*s* is not as large as this, but it is still quite substantial in chemical terms: 6421cm^{-1} = 0.8 eV = 77 kJ mol^{-1}.

Let’s summarize the steps so far in calculations of electronic structure:

1. Born-Oppenheimer approximation (clamped nuclei) to separate electronic from nuclear motion.
2. Independent-electron approximation (central-field approximation in the case of atoms): each electron moves in a potential which is an *average* of the interactions with the other electrons. Quantitative calculations via the Self-Consistent Field (SCF) method.
3. Apply the Pauli principle: make the wavefunction antisymmetric with respect to exchange of electrons. (This step is incorporated into the SCF procedure for quantitative calculations.)
4. Antisymmetrisation leads to Fermi holes (qualitative picture) preventing the close approach of pairs of electrons of the same spin and reducing the repulsion energy between them. The exchange integral provides the quantitative description of this effect.

Consequences of electron repulsion

In the independent-electron picture of an atom, each electron has well-defined angular momentum quantum numbers l, m_l, s and m_s.

In the real atom, the electrons repel one another, so they can exchange orbital angular momentum. Consequently the orbital angular momentum of an individual electron is no longer well defined, and we can only consider the *total* orbital angular momentum, through the quantum numbers L and M_L.

While the spin is not directly affected by electron repulsion, the interplay between orbital and spin angular momentum that results from the Pauli principle means that it is not useful to think about individual electron spins either, so we can only use the total spin, with quantum numbers S and M_S.

To reduce the electron repulsion energy as much as possible, we need as many Fermi holes as possible, which in turn means as many parallel electron spins as possible.

Hund’s Rules

These considerations lead to *Hund's First Rule:* for the ground configuration of an atom, the term that is lowest in energy has the maximum possible S.

More detailed consideration of electron repulsion also leads (for less obvious reasons) to *Hund's Second Rule*: if there is more than one term with the maximum S, the one with maximum L lies lowest, where L is the total orbital angular momentum quantum number.

These rules apply, strictly speaking, *only to the ground configuration* of an atom or atomic ion. They can give a useful guide for higher-energy configurations, but should not be relied on in such cases.

To clarify these rules, we need to understand the technical expressions *term* and *configuration*.

Configurations, terms and levels

A *configuration* of an atom or molecule simply specifies which orbital shells contain electrons. For the He atom, the ground (lowest-energy) configuration is $1s^2$; the excited configurations include $\mathrm{l}s2s$ and $\mathrm{l}s2p$. The ground configuration of the C atom is $\mathrm{l}s^2 2s^2 2p^2$.

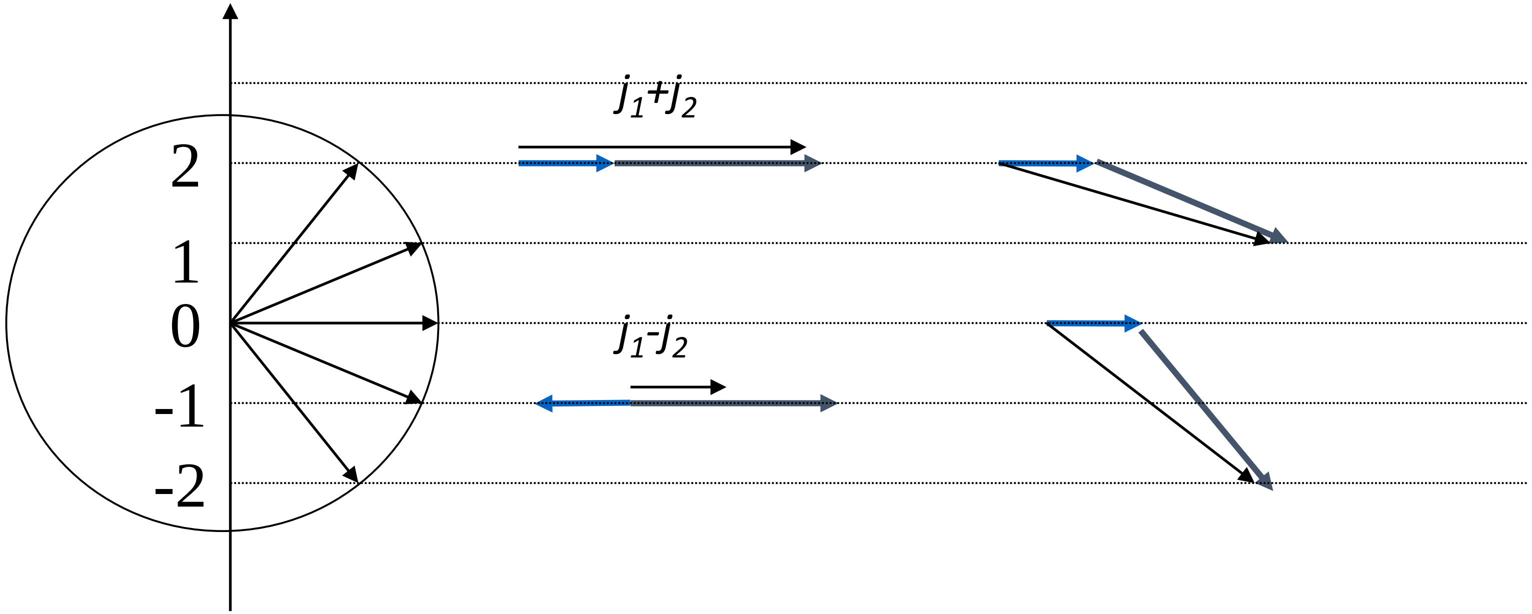
The electrons have both orbital and spin angular momenta. The total orbital angular momentum is called $\boldsymbol{L}$; since it is an angular momentum there are quantum numbers L and M_L, with M_L taking values $L, L - 1, \ldots, -L$. Because the orbital wavefunctions have to be single-valued these quantum numbers are integers.

In the same way, there is a total spin $\boldsymbol{S}$, with quantum numbers S and M_S (which may be half-odd-integers). The values of L and S define a *term.*

A. Addition of two angular momenta:

The addition of two angular momenta characterized by quantum number j_1 and j_2 results in a total angular momentum whose quantum number J has the possible values:

$J=j_1+j_2, j_1+j_2-1, \dots, |j_1-j_2|$



B. The total electronic orbital angular momentum

The total electronic orbital angular momentum of an n-electron atom is defined as the vector sum of the angular momenta of the individual electron:

$$\vec{L} = \sum_i \vec{m}_l(i)$$

The total-electronic-orbital-angular-momentum quantum number L of an atom is indicated by a code letter:

L	0	1	2	3	4	5	6	7
Letter	S	P	D	F	G	H	I	K

For a fixed L value, the quantum number M_L ($M_L\hbar$---the z component of the total electronic orbital angular momentum) takes on 2L+1 values ranging from –L to L.

Orbital symbol

$$\hat{l}\,\psi_i = \sqrt{l_i\left(l_i+1\right)}\hbar\psi_i$$

$$\hat{l}_z\psi_i = m_l\hbar\psi_i$$

l	0	1	2	3	4	5	6	7
Letter	s	p	d	f	g	h	i	k

Term symbol

$$\hat{L}\Psi = \sqrt{L\left(L+1\right)}\hbar\Psi$$

$$\hat{L}_z\Psi = M_L\hbar\Psi$$

L	0	1	2	3	4	5	6	7
Letter	S	P	D	F	G	H	I	K

$$M_L = -L, -L+1, \dots, L$$

$$(2L + 1)$$

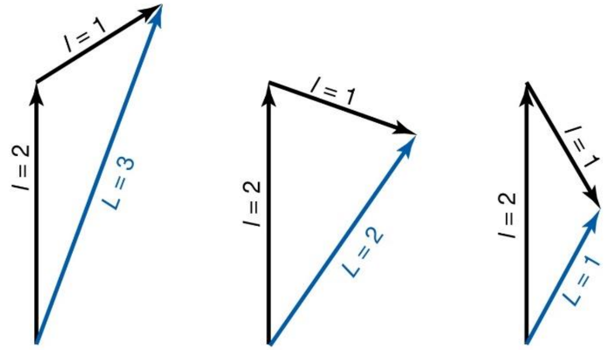
Example: Find the possible values of the quantum number L for states of carbon atom that arise from the electron configuration $1s^2 2s^2 2p3d$.

Solution:

d^1p^1

s	*l=0*
p	*l=1*
d	*l=2*

Angular momentums are vectors



The total-orbital-angular-momentum quantum number ranges from 1+2 = 3 to |1-2| = 1

L = 3, 2, 1

C. The total electronic spin angular momentum

The total electronic spin angular momentum **S** of an n-electron atom is defined as the vector sum of the spins of the individual electron:

$$\vec{S} = \sum_i \vec{m}_s(i)$$

For a fixed S value, the quantum number M_S takes on 2S+1 values ranging from –S to S.

Example: Find the possible values of the quantum number S for states of carbon atom that arise from the electron configuration $1s^2 2s^2 2p 3d$.

Solution:

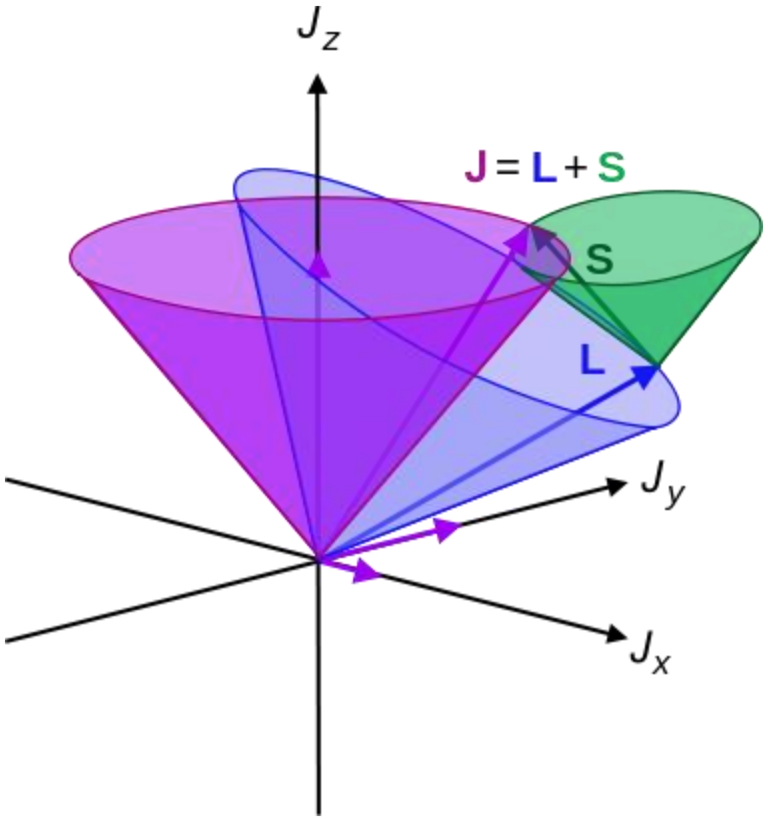
1s electrons: $M_s = +\frac{1}{2} - \frac{1}{2} = 0$

2s electrons: $M_s = +\frac{1}{2} - \frac{1}{2} = 0$

2p electrons: $m_s = \frac{1}{2}$ *3d electrons:* $m_s = \frac{1}{2}$

Addition of two angular momenta rule S = 1, 0

Finally, there is an overall total angular momentum $\boldsymbol{L} + \boldsymbol{S}$, which is called $\boldsymbol{J}$. The quantum number J associated with the total angular momentum can take the values $L + S, L + S - 1,$ ..., down to $|L - S|$. The values of L, S and J define a *level*. If $S \leq L$, which is often the case, there are $2S + 1$ values of J, i.e. $2S + 1$ levels, so $2S + 1$ is called the *multiplicity* of the term (whether or not $S \leq L$).



The total angular momentum

$$J = (L + S),\ (L + S) - 1, \ldots |L - S|$$

Spin – orbit coupling

Example: Find the possible values of the total-angular- momentum quantum number resulting from the addition of two angular momenta with quantum number $j_1 = 2$ and $j_2 = 3$.

Solution: $j_1+j_2=2+3=5$

$|j_1-j_2|=|2-3|=1$

The possible J values are: 5, 4, 3, 2, 1

Example: Find the possible values of the total-angular- momentum quantum number resulting from the addition of two angular momenta with quantum number $j_1 = 2$ and $j_2 = 3/2$.

Solution: $j_1+j_2=2+3/2=7/2$

$|j_1-j_2|=|2-3/2|=1/2$

The possible J values are: 7/2, 5/2, 3/2, 1/2

Term symbols

This information is presented in the form of a *term symbol.*

The central item represents the quantum number L, but it is expressed as a letter: S, P, D, F, etc., for $L = 0, 1, 2, 3$, etc. It is conventional to use lower-case letters for one-electron properties and upper-case for many-electron properties, and these letters follow the scheme used for one-electron orbital angular momenta

multiplicity → $^{2S+1}L_J$ total angular momentum quantum number J

For example, the B atom has the configuration ls^22s^22p. Completely filled shells have total angular momentum zero, so we need only consider the $2p$ electron. It has $l = 1$ (so $L = 1$, symbol P) and $s = \frac{1}{2}$ (so $S = \frac{1}{2}$ and the multiplicity is 2 — a doublet). J can be $L + S = \frac{3}{2}$ or $L + S - 1 = |L - S| = \frac{1}{2}$. There are two *levels,* with term symbols $^2P_{1/2}$ and $^2P_{3/2}$.

Spin-orbit coupling and level splittings

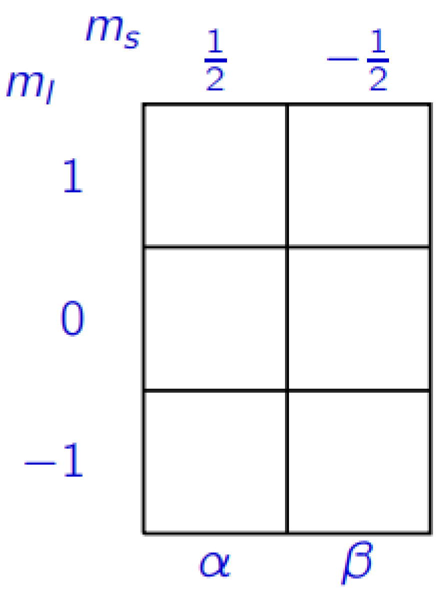
The levels of a term have slightly different energies as a result of *spin-orbit coupling*. There is an interaction between the magnetic moment of each electron, which is proportional to its spin, and its own orbital motion. There is a slight preference for the spin of each electron to be in the opposite direction to its own orbital angular momentum, and for shells that are less than half full the result is that the lowest-energy level is the one with smallest J.

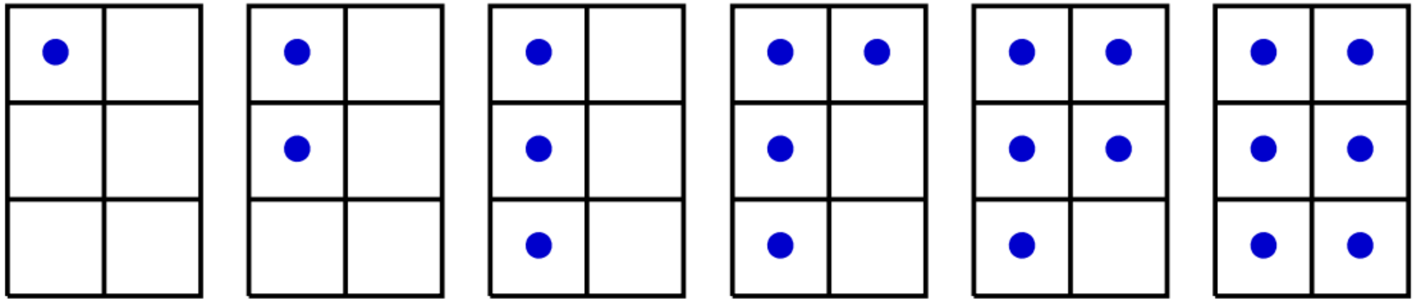
For shells that are more than half full, the lowest-energy level is the one with the largest J. These assertions about the J value for the lowest level constitute *Hund's third rule*.

Ground terms of atoms

Finding the ground term of an atom or ion is relatively simple, because of Hund's rules. M_S takes values from S to $-S$, so the highest possible value of S is the same as the highest possible value of M_S. To evaluate M_S we just count $\frac{1}{2}$ for each α electron and $-\frac{1}{2}$ for each β. To get the highest possible M_S we have to fill α-spin orbitals first, before filling any β-spin ones. Similarly the highest possible value of L is the same as the highest possible value of M_L, which is the sum of m_l values for the individual electrons. To get the highest M_L we fill the orbitals with the highest m_l first.

For p electrons, we have six 'boxes' for electrons, labelled by m_l and m_s. We fill the α boxes first, then the β, in each case filling the boxes with the highest m_l first.





	B	C	N	O	F	Ne
$M_L=$	1	1	0	1	1	0
$M_S=$	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
Term:	$^2P_{1/2}$	$^3P_0$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^1S_0$

We can find the ground terms of ions in the same way. The positive ion of element Z has the same number of electrons, and therefore the same ground term, as the neutral atom $Z-1$. The same method is used for atoms and ions with d^n configurations. The only difference is that m_l runs from 2 to -2.

Anomalous ionization energies

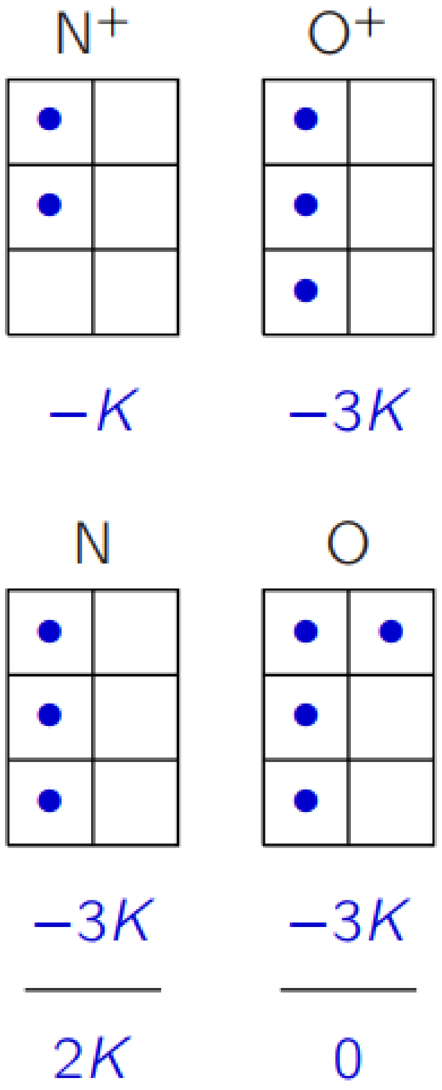
We can now understand the blips in the graph of ionization energies between N and O and between P and S.

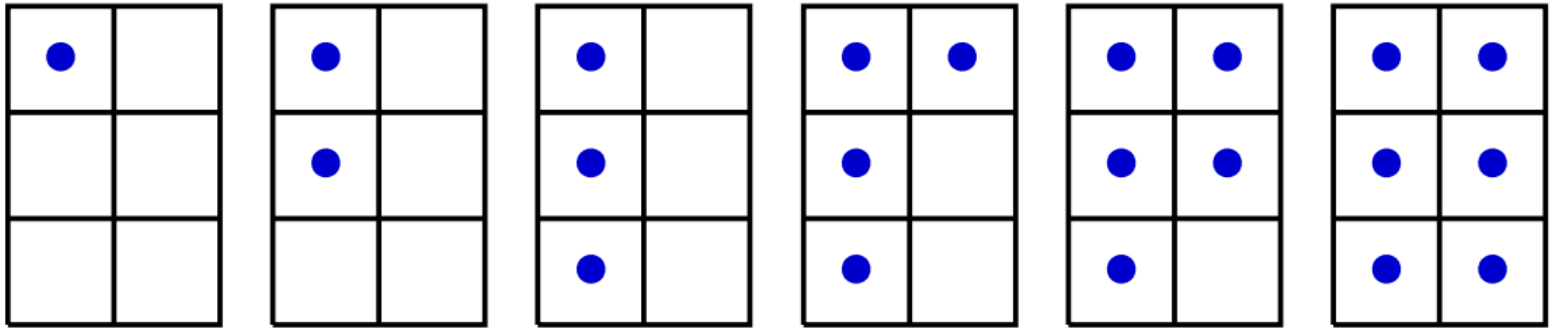
The N atom has ground term ^4S. Its positive ion, N^+, has ground term ^3P, like the C atom. The O atom has ground term ^3P, and O^+ has ground term ^4S.

Now if we add an electron to N^+, it has the same spin as the two p electrons already there, and there is a Fermi hole and a favourable exchange integral for each electron repulsion.

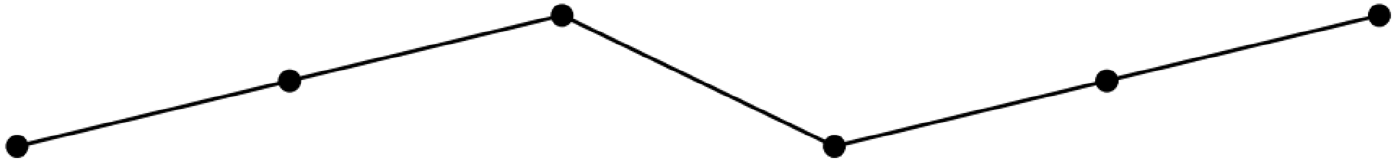
If we add an electron to O^+, however, it has to have opposite spin to the ones already there, so there are no new Fermi holes. Consequently the O atom has a higher energy relative to O^+ than the N atom relative to N^+.

This is the reason why O has a smaller ionization energy than N.





	B, C⁺	C, N⁺	N, O⁺	O, F⁺	F, Ne⁺	Ne
M_L=	1	1	0	1	1	0
M_S=	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
Term:	$^2P_{1/2}$	$^3P_0$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^1S_0$
Exchange energy:	0	-K	-3K	-3K	-4K	-6K
ΔE_{exch}: (ion - atom)	0	K	2K	0	K	2K



More on spin-orbit coupling

The *spin-orbit coupling* is not described by the Schrodinger Hamiltonian, because it is relativistic in origin, but we can add it in. The spin-orbit coupling energy for a single electron is $\zeta \boldsymbol{l} \cdot \boldsymbol{s}$, with $\zeta > 0$. For a many-electron atom, the spin-orbit energy within a single term takes the form $\lambda \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$, where $\lambda = \pm\zeta/2S$. The plus sign applies for shells that are less than half full, and the minus sign for shells that are more than half full.

The total angular momentum *is* $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$, which is associated with the quantum number J. J can take the values from $L + S$ by integer steps down to $|L - S|$, as we have seen.

Now

$$\hat{\boldsymbol{J}}^2 = \left(\hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}\right)^2 = \hat{\boldsymbol{L}}^2 + 2\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} + \hat{\boldsymbol{S}}^2$$

so

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2\right)$$

For an atomic term, $\hat{\boldsymbol{L}}^2$ has the eigenvalue $L(L+1)$ and $\hat{\boldsymbol{S}}^2$ has the eigenvalue $S(S+1)$, while $\hat{\boldsymbol{J}}^2$ has the eigenvalue $J(J+1)$, which is different for each level.

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_i(r_i)$$

H_0 still can not interpret the atomic spectrums. We must consider the high level Hamiltonian

$$\hat{H}_0 = \hat{H}_0 + \hat{H}_{\text{SO}} \qquad \hat{H}_{\text{SO}} = \sum_i \xi(r_i)\,\hat{\mathbf{L}}_i\cdot\hat{\mathbf{S}}_i$$

H_0 commutes with L and with S, but H does not

$$\boxed{\begin{aligned}&\left[\hat{L}_Z,\hat{L}\cdot\hat{S}\right] = \left[\hat{L}_Z,\left(\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z\right)\right]\\ &= \left[\hat{L}_Z,\hat{L}_x\right]\hat{S}_x + \left[\hat{L}_Z,\hat{L}_y\right]\hat{S}_y + 0\\ &= i\hbar\left(\hat{L}_y\hat{S}_x - \hat{L}_x\hat{S}_y\right) \neq 0\end{aligned}}$$

$$\boxed{\begin{aligned}&\left[\hat{S}_Z,\hat{L}\cdot\hat{S}\right] = \left[\hat{S}_Z,\left(\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z\right)\right]\\ &= \left[\hat{S}_Z,\hat{S}_x\right]\hat{L}_x + \left[\hat{S}_Z,\hat{S}_y\right]\hat{L}_y + 0\\ &= i\hbar\left(\hat{L}_x\hat{S}_y - \hat{L}_y\hat{S}_x\right) \neq 0\end{aligned}}$$

$$\boxed{\begin{aligned}&\left[\hat{J}_Z,\hat{L}\cdot\hat{S}\right] = \left[\left(\hat{L}_Z + \hat{S}_Z\right),\hat{L}\cdot\hat{S}\right]\\ &= \left[\hat{L}_Z,\hat{L}\cdot\hat{S}\right] + \left[\hat{S}_Z,\hat{L}\cdot\hat{S}\right] = 0\end{aligned}}$$

H_0, L^2, L_Z

have the common eigenfunctions $R(r_i)Y_{lm_l}(\theta_i,\varphi_i)$

S^2, S_Z

have the common eigenfunction $\sigma_{ms}(i)$

H_0, L^2, L_Z, S^2, S_Z

have the common eigenfunction $\psi_{nlm_lm_s}(i)=R(r_i)Y_{lm_l}(\theta_i,\varphi_i)\sigma_{ms}(i)$

$H\ (H_0+L\cdot S)$, L^2, S^2, J^2, J_z

have the common eigenfunctions, l,s, j, m_j are the good quantum numbers

Hund's third rule and the Landé interval rule

Consequently the spin-orbit coupling energy takes the form

$$E_J = \left\langle \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \right\rangle = \frac{1}{2}\lambda \left\langle \hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2 \right\rangle = \frac{1}{2}\lambda [J(J+1) - L(L+1) - S(S+1)]$$

Since λ is *positive* for shells that are less than half full, but *negative* for shells that are more than half full, this leads to *Hund's third rule* :

> If the shell is less than half full, the lowest level within the ground term is the one with minimum *J*; if it is more than half full, the lowest level is the one with maximum *J*.

The scalar product **S·L** is negative if the spin and orbital angular momentum are in opposite directions. Since the coefficient of **S·L** is positive, lower J is lower in energy.

This result also leads to the *Landé interval rule*: the splitting between adjacent levels is proportional to the higher J value:

$$E_{J+1} - E_J = \frac{1}{2}\lambda[(J+1)(J+2) - J(J+1)] = \lambda(J+1)$$

The *spin-orbit coupling constant* λ increases sharply with atomic number; for instance it is about 270 cm^{-1} for F, 586 cm^{-1} for Cl and 2460 cm^{-1} for Br. If the value is too large, so that the effects of spin-orbit coupling are comparable with those of electron repulsion, the treatment given here (known as *Russell-Saunders coupling)* is inappropriate.

The following approach may help in understanding Hund's third rule.

For the B atom, a single electron with $m_s = \frac{1}{2}$ and $m_l = 1$ has $M_J = ML + M_S = m_l + m_s = \frac{3}{2}$, so this microstate belongs to the level with $J = \frac{3}{2}$. The spin and orbital angular momenta are in the same direction, so this arrangement is unfavourable.

In the fluorine atom with the arrangement shown, we again have $M_L = 1, M_S = \frac{1}{2}$ and $M_J = \frac{3}{2}$, so again this microstate belongs to the level with $J = \frac{3}{2}$. However the spin-orbit contributions for the two electrons with $m_l = 1$ cancel (one has spin up, the other spin down), and similarly for the two with $m_l = 0$. The remaining electron has $m_l = -1$ and $m_s = \frac{1}{2}$, so the spin and orbital angular momenta are in opposite directions and this arrangement is favourable.

The energy differences involved are quite small for light atoms (400 cm^{-1} for fluorine). They become much more important for heavier atoms.