Molecular Term Symbols
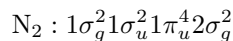
A molecular *configuration* is a specification of the occupied molecular orbitals in a molecule. For example,

$$\text{N}_2 : 1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$$

A given configuration may have several different *states* depending on how the electrons are arranged in the valence orbital(s); a molecular term symbol labels these states and specifies the total spin and orbital angular momentum of the molecule, along with various other symmetries:

$$^{2S+1}|\Lambda|_{(g/u)}^{(+/-)}$$

The various symbols here have the following meanings:

- S is the *total spin angular momentum quantum number*, formed from the individual electrons' spin quantum numbers, $s_i = \frac{1}{2}$, from the Clebsch-Gordan series, as for atomic term symbols. For one unpaired electron, $S = s_1 = \frac{1}{2}$ (a *doublet* state with $2S + 1 = 2$); for two unpaired electrons the possible values are $S = s_1 + s_2 = 1, S = s_1 + s_2 - 1 = 0$, giving *triplet* ($2S + 1 = 3$) and *singlet* ($2S + 1 = 1$) states respectively. A *closed-shell* configuration is necessarily a singlet state;

- Λ is the quantum number for the *total orbital angular momentum of the electrons about the internuclear axis*. Unlike in atoms, the cylindrical symmetry created by the strong electric field of the nuclei in a linear molecule destroys the relationship $[\hat{H}, \hat{L}^2] = 0$, and so L ceases to be a good quantum number. Instead, we can use the quantum number Λ, corresponding to the component of L along the internuclear (z-) axis:

$$\Lambda = \sum_i \lambda_i$$

  where λ_i is equal to 0 for a σ electron, and ± 1 for a π electron. $|\Lambda| = 0, 1, 2, 3, \dots$ is written $\Sigma, \Pi, \Delta, \Phi, \dots$. Note that in this context, it is better to think of the degenerate π orbitals as the pair (π_+, π_-), where the $+$ and $-$ subscripts represent clockwise and anticlockwise rotation ($\hat{L}_z \pi_\pm = \pm\hbar\pi_\pm$), rather than the functions (π_x, π_y). The latter (real) functions are linear combinations of the former with the same energy but they are not eigenfunctions of the $\hat{L}_z$ operator, so they do not contain the necessary information about λ;

- the g/u subscript applies only to molecules with a centre of symmetry and labels the symmetry of the electronic wavefunction with respect to inversion through this centre;

- the $+/-$ superscript applies only to Σ states, and labels the symmetry of the electronic wavefunction with respect to reflection in a plane containing the nuclei.

For the ground state configurations of first row diatomic molecules, term symbols are deduced as follows:

Closed-shell configurations

This is the easy case; all electrons are paired off in closed orbitals, *e.g.*

$$F_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$$

so there is no net orbital or spin electronic angular momentum: $S = 0$, $\Lambda = 0$ and the term symbol is
$$^1\Sigma_g^+$$

One unpaired σ-electron

$S = \frac{1}{2}$, and $\Lambda = 0$, so we have a $^2\Sigma^+$ term, *e.g.*

$$N_2^+ : 1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1$$

has the molecular term symbol:
$$^2\Sigma_g^+$$

One or three π-electrons

The one unpaired electron $(S = \frac{1}{2})$ is in a π-orbital, so $|\Lambda| = 1$, and the term symbol is $^2\Pi$. For example,

$$B_2^+ : 1\sigma_g^2 1\sigma_u^2 1\pi_u^1$$

gives rise to the term symbol:
$$^2\Pi_u$$

For three π electrons (*e.g.* O_2^-), the configuration can be thought of as either $\pi_+^2 \pi_-^1$ (giving $\Lambda = +1 + 1 - 1 = +1$) or $\pi_-^2 \pi_+^1$ (giving $\Lambda = -1 - 1 + 1 = -1$). In both cases, $|\Lambda| = 1$ and $S = \frac{1}{2}$, and the term symbol is the same as for a π^1 configuration.

Two (identical) π-electrons

For example, O_2, B_2. The easy way is to note that the states arising from a π^2 configuration will have symmetries given by the direct product of the Π irreps of the $D_{\infty h}$ molecular point group:

$$\Pi \otimes \Pi = \Sigma^+ \oplus [\Sigma^-] \oplus \Delta$$

Here, [ ] indicates the antisymmetrized product. The total electronic wavefunction, $\psi = \psi_{\text{spatial}}\psi_{\text{spin}}$ must be antisymmetric (electrons are fermions), so the Σ^- (spatial) part is associated with the *triplet* (symmetric) spin part and the Σ^+ and Δ parts are associated with *singlet* (antisymmetric) spin parts; the term symbols are therefore:
$$^3\Sigma^-, \quad ^1\Sigma^+, \quad ^1\Delta$$

A longer way around is to construct suitably-symmetrized wavefunctions for the states derived from the electronic configuration. For example, the ground state configuration of molecular oxygen is:

$$O_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$$

Let the degenerate valence π MOs be called π_+ and π_- corresponding to opposite rotations of the electron around the internuclear axis. Consider the state in which both electrons occupy π_+, and hence $\Lambda = +2$:

$$\psi_{\text{spatial}}^{(a)} = \pi_+(1)\pi_+(2)$$

This wavefunction is symmetric with respect to permutation of the (identical) electrons, and so must be associated with the *antisymmetric* spin wavefunction. This is the singlet state ($S = 0$):

$$^1\psi_{\text{spin}} = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

The term symbol corresponding to the total wavefunction $\psi_{\text{spatial}}\psi_{\text{spin}}$, is therefore:

$$^1\Delta_g : \pi_+(1)\pi_+(2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

(of course, $\psi_{\text{spatial}} = \pi_-(1)\pi_-(2)$, for which $\Lambda = -2$, gives rise to the same term symbol: the $^1\Delta_g$ state is doubly degenerate).

If we place one electron in each of π_+ and π_-, giving $\Lambda = +1 - 1 = 0$ and a Σ term, we must be careful to construct appropriately symmetrized spatial wavefunctions: $\pi_+(1)\pi_-(2)$ won't do because it does not have a definite symmetry with respect to permutation of the identical electrons. We can have:

$$\psi_{\text{spatial}}^{(b)} = \frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) + \pi_-(1)\pi_+(2)\right]$$

which is symmetric, and hence goes with the singlet spin wavefunction:

$$^1\Sigma_g : \frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) + \pi_-(1)\pi_+(2)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Or we can have:

$$\psi_{\text{spatial}}^{(c)} = \frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)\right]$$

which is antisymmetric, and hence can go with one of the three symmetric triplet spin wavefunctions:

$$^3\Sigma_g : \frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)\right]\begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \\ \beta(1)\beta(2) \end{cases}$$

Now, the $+/-$ superscript on these Σ states labels the symmetry of the wavefunction with respect to reflection in any plane containing the nuclei (the operation $\hat{\sigma}$). Such a reflection sends a clockwise rotation to an anti-clockwise

rotation and vice versa, and so interchanges π_+ and π_-. For example,

$$\hat{\sigma}\psi_{\text{spatial}}^{(c)} = \hat{\sigma}\frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)\right]$$

$$= \frac{1}{\sqrt{2}}\left[\pi_-(1)\pi_+(2) - \pi_+(1)\pi_-(2)\right]$$

$$= -\psi_{\text{spatial}}^{(c)}$$

Similarly,

$$\hat{\sigma}\psi_{\text{spatial}}^{(b)} = \psi_{\text{spatial}}^{(b)}$$

Thus, the term symbols are:

$$^3\Sigma_g^-, \quad ^1\Sigma_g^+, \quad ^1\Delta_g$$

Note that the $^1\Delta_g$ state does not have a $+/-$ label: the $\hat{\sigma}$ reflection interchanges the degenerate $\pi_+(1)\pi_+(2)$ and $\pi_-(1)\pi_-(2)$ functions, so degenerate parity-conserved spatial wavefunctions, $\frac{1}{\sqrt{2}}[\pi_+(1)\pi_+(2) \pm \pi_-(1)\pi_-(2)]$, can be constructed. This means that the $^1\Delta_g$ state consists of one '+' and one '-' state, and could be written $^1\Delta_g^{\pm}$, but in practice the $\pm$ is usually omitted.

Spin-orbit coupling

Terms with electronic orbital angular momentum ($|\Lambda| > 0$) and spin angular momentum ($S > 0$) can undergo spin-orbit coupling; the component of the *total* angular momentum along the internuclear axis, Ω, is given as a subscript to the term symbol. For example, the NO molecule has a $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$ electronic configuration and so a $^2\Pi$ term symbol ($S = \frac{1}{2}$ and $\Lambda = \pm 1$). The *spin* angular momentum can make a projection $S_z \equiv \Sigma = \pm\frac{1}{2}$ onto the internuclear axis, and the quantum numbers Λ and Σ add to give $\Omega = \Lambda + \Sigma$:

$$\Omega = +1 + \tfrac{1}{2} = \tfrac{3}{2}$$
$$\Omega = +1 - \tfrac{1}{2} = \tfrac{1}{2}$$
$$\Omega = -1 + \tfrac{1}{2} = -\tfrac{1}{2}$$
$$\Omega = -1 - \tfrac{1}{2} = -\tfrac{3}{2}$$

Therefore, the spin-orbit *levels* are $\Omega = \pm\frac{3}{2}$ and $\Omega = \pm\frac{1}{2}$ (each is doubly degenerate, since the total electronic angular momentum can be clockwise or anticlockwise about the internuclear axis); these are denoted $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$. The splitting is about 120 cm^{-1}, somewhat smaller than $k_\text{B}T$ at room temperature (207 cm^{-1}).

Energy ordering

Hund's rules are a useful guide to the energy ordering of terms *arising from the ground state electron configuration*:

1. **The term with the highest spin multiplicity, $2S + 1$, is lowest in energy.** This is often explained in terms of electron spin correlation: electrons with parallel spins have a tendency to spend more time further apart, on average, than those with paired spins.

2. **For terms of the same multiplicity, the term with the largest orbital angular momentum, given by Λ, is lowest in energy.** A classical explanation of this says that if two electrons orbit the internuclear axis in the same sense (say, clockwise) they will encounter each other less often than if they orbit in opposite senses.

For example, the terms arising from the ground state of O_2 lie in the order $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$.

Selection Rules

Electric dipole allowed transitions between electronic states of linear molecules are subject to the following selection rules:

- $\Delta\Lambda = 0, \pm 1$

- $\Delta S = 0$, in the absence of spin-orbit coupling

- $\Delta\Omega = 0, \pm 1$

- $\Sigma^+ \leftrightarrow \Sigma^+$, $\Sigma^- \leftrightarrow \Sigma^-$

- $g \leftrightarrow u$