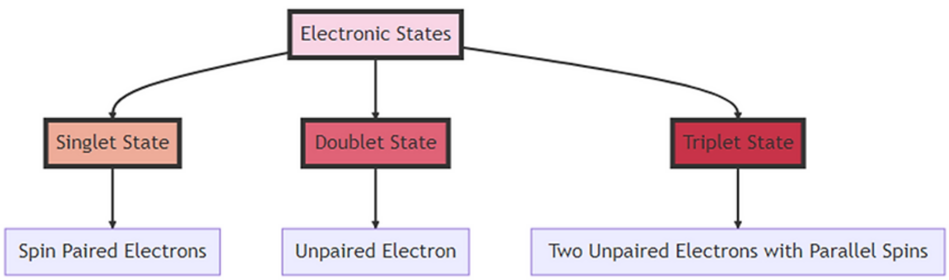
Appendix 1

Concepts of singlet, doublet and triplet electronic states

- The concepts of singlet, doublet, and triplet electronic states are central to the understanding of molecular electronic structure, especially in the context of spectroscopy and photochemistry.
- These terms primarily refer to the spin states of electrons in atoms or molecules.



1. Electron Spin:

- Electrons possess an intrinsic angular momentum called spin, which can take on one of two possible values: +½ or -½ (often referred to as "spin up" and "spin down").

2. Pauli Exclusion Principle:

- No two electrons in a single atom can have the same set of quantum numbers. This means, for instance, that two electrons occupying the same molecular orbital must have opposite spins.

3. Multiplicity:

- Multiplicity is defined as 2S+1, where S is the total spin quantum number.

- The total spin quantum number, S, is the sum of the individual spins of all unpaired electrons in the system.

Singlet, Doublet, and Triplet States:

1. Singlet State:

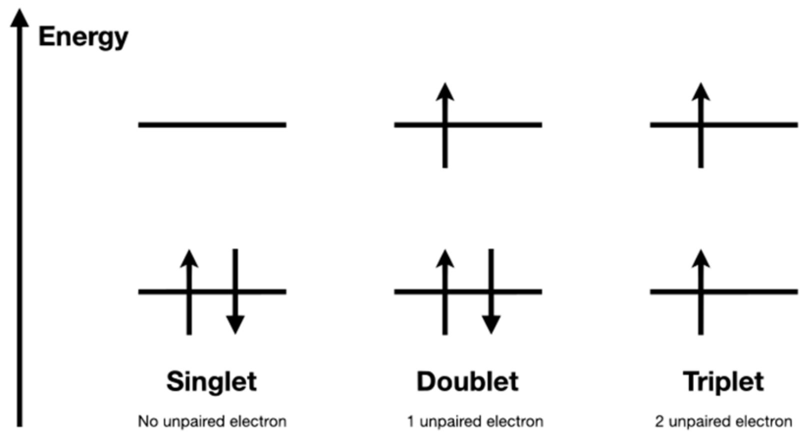
- There are no unpaired electrons.
- All electrons are spin-paired (e.g., in a filled molecular orbital).
- Total spin $S = 0$; hence, **Multiplicity = 2(0) + 1 = 1.**
- Often denoted as ^1X, where X represents the type of electronic state (e.g., ^1S for a singlet ground state).

2. Doublet State:

- There's one unpaired electron.
- Total spin $S = \frac{1}{2}$; hence, **Multiplicity = 2(½) + 1 = 2.**
- This is commonly seen in radicals.
- Often denoted as ^2X, where X represents the type of electronic state.

3. Triplet State:

- There are two unpaired electrons with parallel spins (both "spin up" or both "spin down").
- Total spin $S=1$; hence, **Multiplicity = 2(1) + 1 = 3.**
- Often denoted as ^3X, where X represents the type of electronic state.



Atoms in singlet, doublet, and triplet states

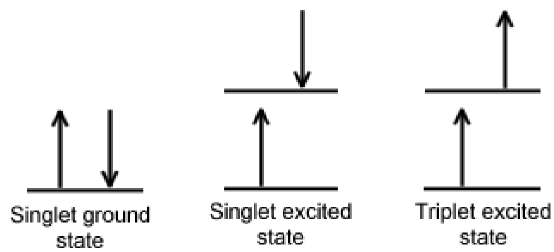
In photochemistry and spectroscopy:

- When a molecule in a singlet ground state absorbs energy (like from a photon), it may be promoted to a higher-energy singlet state.
- If the molecule undergoes a spin flip (where one of the paired electrons changes its spin direction), it can end up in a triplet state, which typically has a longer lifetime than an excited singlet state.
- The transition between singlet and triplet states is "spin-forbidden" according to quantum mechanics, which means that transitions between these states (like phosphorescence) are typically slower than "spin-allowed" transitions (like fluorescence).

Singlet and Triplet Excited State

Understanding the difference between fluorescence and phosphorescence requires the knowledge of electron spin and the differences between singlet and triplet states. The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_i, m_s) and only two electrons can occupy each orbital where they must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules do not exhibit a magnetic field and are diamagnetic. In diamagnetic molecules, electrons are not attracted or repelled by the static electric field. Free radicals are paramagnetic because they contain unpaired electrons have magnetic moments that are attracted to the magnetic field.

A singlet state is defined as a state when all the electron spins are paired in the molecular electronic state and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that can have two possible orientations when exposed to a magnetic field and imparts different energy to the system. A singlet or a triplet can form when one electron is excited to a higher energy level. In an excited singlet state, the electron is promoted with the same spin orientation as it had in the ground state (paired). In a triplet excited stated, the electron that is promoted has the same spin orientation (parallel) as the other unpaired electron. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure below. Singlet, doublet and triplet is derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculated the S for the excited singlet state, the equation would be 2(+1/2 + -1/2)+1 = 2(0)+1 = 1, therefore making the center orbital in the figure a singlet state. If the spin multiplicity for the excited triplet state was calculated, we obtain 2(+1/2 + +1/2)+1 = 2(1)+1 =3, which gives a triplet state as expected.



The difference between a molecule in the ground and triplet excited state is that the electrons are diamagnetic in the ground state and paramagnetic in the excited triplet state. This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) more improbable than the singlet-to-singlet transitions because it involves a spin flip. This singlet to triplet (or reverse) transition involves a change in *electronic* state. For this reason, the lifetime of the triplet state is longer than that of the singlet state by an approximately 10^4 fold difference. Absorption of radiation inducing the transition from ground to excited triplet state has a low probability, thus their absorption bands are less intense than singlet-singlet state absorption. The excited triplet state can be populated from the excited singlet state of certain molecules which results in phosphorescence. These spin multiplicities in ground and excited states can be used to explain transition in photoluminescence molecules by the Jablonski diagram.