Putting a Spin on Photochemical Processes.
The Role of Electron Spin in Photophysical and Photochemical Processes

1. Introduction. Spin Chemistry.

This chapter explores the role of **electron spin** in determining the course of photophysical and photochemical processes. The approach taken to understand electron spin will be analogous to that employed for understanding the role of **electronic orbitals** in determining the course of photophysical and photochemical processes. We shall refer to those quantum mechanical principles which describe the qualitative aspects of electron spin in molecular systems. We shall then consider models which allow the visualization of the qualitative aspects of electron spin by reference to simple systems, i.e., those containing the essence of the physics and chemistry which determines the properties of spin systems that are essential to understanding photochemical and photophysical processes. With these simple **structural models**, and particularly with the **vector model of spin**, we shall employ an "Aufbau Principle" to determine the **number of possible spin states** and the **relative magnetic energies of the possible spin states**. We shall then establish a **dynamic model** to determine the "allowed" and "forbidden" (more realistically the "more probable" and the "less probable") **transitions** between spin states for both radiative and radiationless transitions. We shall also show how the characteristics of spin states can be associated with molecular structure and how measurements of spin characteristics can be employed for the determination of molecular structure of systems possessing one or two orbitally unpaired electrons. Our goal is to develop a useful paradigm for understanding the role of spin, in particular electron spin, in photophysical and photochemical processes.

We shall see that the same paradigm applies to the principles of **magnetic resonance spectroscopy**, a powerful tool for the investigation of photochemical reaction mechanisms. Electron spin resonance (ESR) or nuclear spin resonance (more popularly termed nuclear magnetic resonance, NMR) are forms of spectroscopy in which *radiative* transitions between magnetic energy levels, separated by interactions of spins with an applied static magnetic field, are induced by the magnetic component of elecromagnetic radiation. Intersystem crossings are *radiationless* transitions between magnetic energy levels which differ in spin angular momentum. **Spin chemistry** is a field which evolves from the dependence of the selection rules for intersystem crossing on the features of spin angular momentum and from the fact that the elementary steps of making and breaking of chemical bonds (or electron transfers) must preserve spin angular momentum (Wigner's Rules).

The principles of magnetic resonance, intersystem crossing and spin chemistry are all interrelated through the principles of **spin angular momentum** and the relationships between spin angular momentum and **magnetic moments**. Interactions between magnetic moments provide a clear general physical model for the magnetic energy levels and possible the transitions between magnetic energy levels. We need a model which will allow visualization of spin angular momentum and magnetic moments and which provides a basis for understanding spin chemistry and magnetic resonance spectroscopy.

Visualization of Spin Chemistry.

It is generally accepted that the most elegant, proper and effective way to do science is to do it mathematically. However, when learning a subject that is highly mathematical, it is often difficult to appreciate what is going on and the mathematics may become an intellectually sterile "black box" for getting the "correct" answer. Quantum mechanics is a subject that requires considerable mathematical sophistication for its quantitative use. It is not possible to understand molecular photochemistry without the liberal and essential use of ideas from quantum mechanics. However, the approach taken in this text, as in its predecessors, is that much of the mathematics of quantum mechanics can be reasonably visualized and interpreted in terms of pictures that capture the qualitative aspects of the phenomena under consideration. Such visualization of the mathematics of quantum mechanisms can be quite an intellectual treat as the imagination creates a "motion picture" of the choreography of structural and dynamic events imagined to occur at the microscopic level. Such visualizations, like all analogies and models, are an incomplete and imperfect representation of the "correct" mathematical representations and complete mathematics, but one must remember that chemical systems are always so complicated that the "correct" representations are rarely used. Indeed, it may safely be said that no mathematic representation of any complex chemical phenomenon is ever truly complete and the shortcuts and approximations employed to mathematically represent complex chemical phenomena are sometimes more intellectually compromising and less informative than resorting to imperfect physical pictures.

In defense of the pictorial approach, it is sometimes useful to approach the effectiveness of the language of mathematics by creating pictures which are themselves mathematical objects. For example, **the use of vectors simultaneously provides both clear and precise visualization of quantities and dynamic processes and a useful matrix of mathematical rules and procedures.** When such is the case, the power of visualization and insights that it can provide more than compensate for potential pitfalls of a qualitative mathematical treatment. Chemists, in particular, have sought visualization and verbal interpretations of quantum mechanics, features that are emphasized in this text.

Spin. Angular Momentum and Magnetic Moments

What is electronic spin? The **spin** of a fundamental microscopic particle such as an electron (or a nucleus) is associated with a quantity termed its **intrinsic spin angular momentum**. Thus, to understand and appreciate the qualitative and quantitiative aspects of spin we must appeal to the aspects of angular momentum. We therefore ask, what is angular momentum at the microscopic scale of fundamental particles of an atom? Classically, **angular momentum is a property of a macroscopic object which is in a state of rotation about an axis.** At the quantum mechanical or microscopic level, spin is a fixed characteristic of a fundamental particle, similar to the charge or mass of an electron or proton. For example, an electron possesses a fixed and characteristic spin angular momentum of 1/2\ (\, Planck's constant divided by 2π, is the fundamental quantum mechanical unit of angular momentum) whether it is a "free" electron which is not associated with any nucleus, or whether the electron is associated with a nucleus in an atom, a molecule or a radical. The spin angular momentum of an electron is the same whatever orbital the electron happens to occupy. At this point we simply note that although spin is a quantum property of electrons, **we still can profitably visualize spin by resorting to a classical analogy of a spherical object executing a spinning motion about an axis, i.e., a top or a gyroscope.**

It is important to emphasize that certain nuclei, such as a proton or a ^{13}C nucleus also possess spin, namely, 1/2 \ exactly the same amount as an electron! This equivalence of angular momentum of all "sspin 1/2 particles" will be of critical importance for understanding certain intersystem crossing processes and magnetic resonance phenomena. For example, we shall see that the spins of certain nuclei can also play an important role, especially in determining the chemical reactivity of radical pairs and biradicals. We shall also be interested in the structure and dynamics of the electron's spin and how the electron spin in a molecule or radical interacts with its own molecular structure, with molecules in its environment, with applied laboratory magnetic fields, and with applied oscillating electromagnetic radiation.

Visualization of the characteristics of electron spin will come from the development of a model which associates specific **magnetic properties**, i.e., a **magnetic moment**, with the electron's **spin angular momentum**. To visualize electron spin and its associated magnetic moment, we shall appeal to a specific model that will allow the development of a **vector representation of electron spin**. We shall then relate the properties of this model to experimental properties and various aspects of molecular structure. With the vector model we will be able to visualize and qualitatively interpret all of the key structrural and dynamic properties involving the **number and energetic ordering of electronic spin states and radiationless and radiative transitions between spin states** that are involved in the general photophysical and photochemical paradigms.

The Spin States and Spin Transitions in the General Photochemical Paradigm.

A simplified, but general, "working" photochemical paradigm (Figure 1) for photophysics and photochemistry of reactions involving photochemical primary processes from the triplet state provides a convenient framework for a discussion of the role of electron spin in molecular photochemistry. In this paradigm, there are at least six states or structures that are typically involved in a complete photochemical process: S_0 (R), S_1(R), T_1(R), ^{3}I, ^{1}I and S_0 (P). In the photophysical paradigm, the reactive intermediate, I, is not involved since no photochemistry occurs. The orbital description of these states is given in Figure 1 (bottom), where the spins of the electrons in the triplet states are loosely shown as "**parallel**" and the spins of the electrons in the singlet states are shown as "**antiparallel** (the meaning of these terms will be defined more precisely in detail below in terms of the vector model). In this discussion we are ignoring photochemical reactions originating from a singlet state, S_1, because for such processes a change in spin is usually not a critical factor in the photochemistry and because the majority of photochemical reactions which have been examined involve the triplet state.

Each of the states in the paradigm can be classified in terms of the **electron configuration** of the two highest energy electrons of the molecules, R and P, or the excited state R* or the intermediate, I (Figure 1, bottom). The **electronic transitions** can be classified in terms of the **orbital structure of the electronic states** occurring when one state is converted to another. Thus, the number of electron states and the transitions between them are conveniently classified in terms of the orbital configuration of the two highest energy electrons. Effectively, all of the other electrons of the molecule are considered passive in this simple model. In an analogous manner, we shall attempt to classify each of the states and possible transitions in terms of the electron spin. In other words, we shall define **spin configurations** which define **spin states**, and classify **spin transitions** between the **spin states** in terms of the **spin structure of the magnetic states.** In the same way that we visualize and classify transitions between electronic states in terms of orbital jumps of electrons, we shall employ the vector model to visualize and classify transitions between magnetic states in terms of vector flips and vector rephasing. Furthermore, in the same manner that only the two highest energy electrons are considered explicitly, only the orbitally unpaired electron spins need be considered explicitly because the spins of a pair of electrons in the same orbital completely compensate each other's angular momentum and magnetic properties.

The basic interactions that determine the number and the structure of the electronic states and the transitions between them are **electrostatic** or **Coulombic** in origin (repulsions and attractions between electronic and nuclear charges), whereas the basic interactions that determine the nature of the spin states are **magnetic** in origin. These magnetic interactions may be represented as the **interactions of a magnetic moment** associated with an electron spin and some other magnetic moment imposed externally (by an applied magnetic field or electromagnetic radiation) or internally (by magnetic moments of other spins or by magnetic moments generated by the orbital motions of electrons). Since **magnetic moments are vector quantities** (i.e., they may be mathematically represented by a **magnitude** and an **orientation** in space) it is plausible to assume that a **vector representation of electron spin** will provide an effective working model for determining the number of spin states and for determining the mechanisms of transitions between spin states.

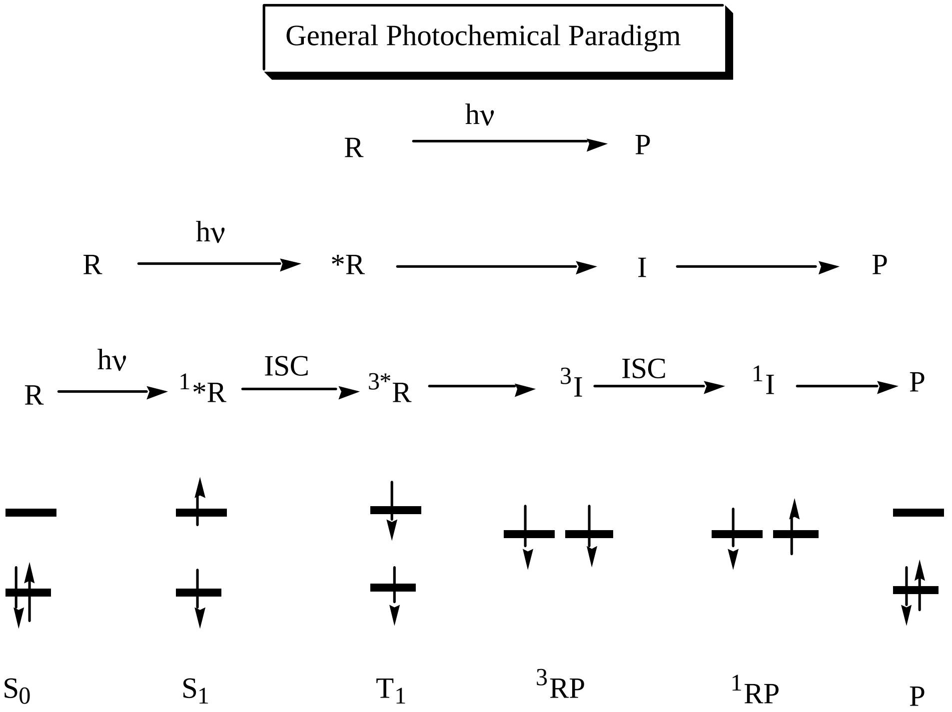

Figure 1. The general photochemical paradigm. Electron spin must be considered in the key transformation involving a spin change for two steps: (1) the molecular S_1 ∅ T_1 ISC and (2) the ISC involving the reactive radical pair, RP, (or biradical) intermediate: ^{3}RP ∅ ^{1}RP. In addition, the theory of electron spin allows us to obtain information on the structure of T_1 and ^{3}RP.

Desirable Features of the Vector Model

Before we develop the vector model, let us briefly indicate the nature of the final conceptual tool we hope to create. First we need to associate some energetic and dynamic features with a structural, i.e., visualizable, model of electron spin. A good model will allow us to enumerate and rank the relative energies of the magnetic configurations and spin states in the same way that we can enumerate and qualitatively rank the relative energy of electronic orbitals and electronic states. The connection of spin structure and energy will come about through the association of spin angular momentum with magnetic moment due to electron spin. The energy of the spin will depend on the interactions of the spin's magnetic moment and other magnetic moments to which it is coupled. These interactions **will influence both the energy of the electron spin and the dynamics of the electron spin**. A successful model will allow us to classify all of the important magnetic interactions in terms of two basic types, a so-called **dipolar interaction** and a **contact interaction** (analogous to the two basic types of electrostatic interactions involving dipolar interaction or overlap interactions) and several couplings or "mechanisms" by which the basic interactions can connect an electron spin to a magnetic moment due to some internal or external source. These mechanisms involve coupling of the magnetic moment due to spin angular momentum and other magnetic moments, which may be "internal" couplings (spin-orbit coupling and spin-spin coupling) or "external" couplings (spin-static magnetic field coupling, spin-electromagnetic field coupling, spin-lattice coupling).