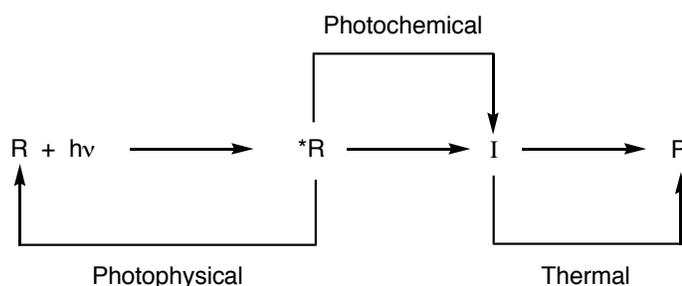


Chapter 2. Electronic, Vibrational and Spin Configurations of Electronically Excited States.

2.1 Visualization of the Electronically Excited Structures in the Paradigms of Molecular Organic Photochemistry

From the working paradigms of Sch. 1.1, 1.2 and 1.3, we have learned that electronically excited states, ($*R$), are critical transient structures in photochemical reactions. Any **chemical** process that is produced directly from R ($*R \rightarrow I, *I, *P, F$) is termed a **primary photochemical process**. Any physical process that proceeds directly from R ($*R \rightarrow R$) is termed a **primary photophysical process**. The most common primary photochemical process for organic molecules is the $*R \rightarrow I$ as shown in Sch. 2.1. The latter is a working paradigm with the addition of the primary photophysical processes $*R \rightarrow R$ (+ heat or + $h\nu$). These photophysical pathways will generally compete with any primary photochemical pathways (Sch. 2.1) that take $*R$ to P , i.e., the primary photochemical process which proceeds through a ground state reactive intermediate I to form P ($*R \rightarrow I \rightarrow P$, shown). For simplicity, the primary photochemical process of Sch. 1.1 that takes $*R$ to P through a funnel without formation of a reactive intermediate ($*R \rightarrow F \rightarrow P$) and the primary photochemical process that takes $*R$ to P by way of electronically excited intermediates ($*R \rightarrow *I, *P \rightarrow P$) are not shown.



Scheme 2.1. The working paradigm for photochemical pathways of $*R \rightarrow P$ and photophysical pathways from $*R \rightarrow R$. See Scheme 1.1 for a more complete paradigm.

The reactive intermediate(s) I undergoes conventional thermal processes ($I \rightarrow P$) leading to the observed product, P. The structure I represents the common reactive intermediates (radical pairs, diradical, carbonium ion/carbanion pairs, zwitterionic species, carbene, etc.). The typical electron structure of I will be discussed in Chapter 6. The thermal pathways from $I \rightarrow P$ are termed *secondary processes* and will be discussed in detail in Chapter 8. "Direct" primary photochemical pathways from $*R \rightarrow F \rightarrow P$ and pathways involving formation of electronically excited state of product (e.g., $*R \rightarrow *I$ and $*R \rightarrow *P$) are known, but turn out to be rare experimentally, and will not be covered explicitly until Chapter 6. The symbols (R, *R, I, P) given in Sch. 2.1 should not be restricted to imply the involvement of single molecular species. For example, it is intended that *R symbolizes the system of reactants which would include any other molecules which are involved in the primary photochemical process. All of the species in Sch. 2.1, including *R, can be represented by traditional Lewis structures and can be discussed in terms of conventional one electron molecular orbitals (MO). It is assumed that the student is familiar with Lewis structural and MO representations of R, P and I, all of which possess the ordinary organic functional groups contained in organic molecules and which discussed in all elementary courses in organic chemistry. It is a goal of the text to make the student comfortable with applying knowledge of the structures of R, P and I towards an understanding of the detailed *electronic, vibrational and spin* structure of *R.

A detailed understanding of primary photophysical and photochemical processes is essential for a proper interpretation and prediction of the plausibility (is a process implied by the paradigm plausible or not?) and probability (how does a given process compete with other processes?) of the individual steps given by Sch. 2.1. An understanding of all these processes is available through the paradigms of the *molecular structure and dynamics of organic molecules*. Quantum mechanics provides the most powerful and effective paradigm of physics and chemistry for the description of molecular structure and dynamics of organic molecules. However, a proper understanding of molecular structure and dynamics through quantum mechanics requires a mathematical sophistication that is well beyond the intended scope and intended readership of this text. This Chapter and Chapter 3 are concerned with the exploitation of the power of quantum mechanical methods by translating the mathematics, which are

required for a rigorous quantum mechanical treatment of organic photochemistry, into pictures and structures that can be more readily comprehended by students who may not have a background or interest in formal mathematics. We will take a pictorial approach which has proven to be very effective: *we shall translate the mathematics of quantum mechanics into pictures that can be translated into molecular structures (this Chapter) and molecular dynamics (Chapter 3)*. This pictorial approach recognizes that the mathematical ideas of quantum mechanics can be interpreted in a *qualitative* manner through pictorial representation and that these representations are understood to always to a certain degree acceptable approximations.

The language of organic chemistry employs pictorial objects termed *molecular structures* to make connections to molecular function, properties and reactivity. The language of quantum mechanics uses mathematical objects termed *wavefunctions* (a term we shall deal with in detail in this Chapter) and the idea of quantized energies to make connections to molecular function, properties and reactivity. Since the molecule is the *same object* being described by both molecular structures and wavefunctions it is natural to expect that there are methods to transform molecule structures into wavefunctions and to transform wavefunctions into molecular structure. Thus in Sch. 2.1, R, *R, I and P may be considered as ordinary molecular structures or as wavefunctions. Visualizations of wavefunctions of R, *R, I and P, although understood to be only approximate models, allow the photochemist's imagination to create a "motion picture" of the choreography of structural, energetic and dynamic events occurring at the molecular level for the overall photochemical transformation of $*R \rightarrow P$.

As in all analogies and models, such visualizations of wavefunctions are incomplete and an imperfect representation of the more "correct" mathematics of quantum mechanics, but such pictures are valid and useful approximations for introducing a student to the concepts of a new field. Indeed, if the pictures provided capture the correct nature of the fundamental structures, the fundamental forces and realistic dynamics of the processes of Sch. 2.1, the student will achieve a valuable introductory and operational knowledge of a field that also will be very helpful as a basis for probing deeper into the subject.

The visualization and pictorial approach to approximations of physical systems is most effective when the "pictures" themselves are/or represent mathematical objects such as those derived from topological or Euclidean geometry (1). For example, the Lewis electron dot structures universally employed by organic chemists to represent molecular structure display the *connectivity* of the atoms in a molecule and the location of valence electrons on (lone pairs) or between (shared pairs) atoms. The Lewis electron dot structures have the properties of a mathematical or topological object, called a *graph*, and displays the graphical relationships between points (atoms) and connections of the atoms with one another with lines (bonds). Indeed, the symbols R, *R, I, *I, *P and P of Sch. 2.1 can be represented as Lewis structures (topological objects or chemical graphs) or as three dimension representations of the position of the atoms in space (Euclidean objects or chemical structures). The organic chemist is very familiar with the topological and Euclidian representation of the structure of organic molecules, i.e., Lewis structures. Even though such structures are, strictly speaking, mathematic abstractions, to the chemist they take on a reality that leads to powerful structure-function, structure-reactivity and structure-property correlations. Understanding that traditional molecular structures are actually abstract mathematical objects may allow the student to be more accepting of the use of wavefunctions as an alternate description of organic molecules.

Is it reasonable to translate wavefunctions into pictures? An a priori justification is as follows. Although wavefunctions are formulated completely in mathematical terms, nevertheless the physical basis for construction of wavefunctions are typically based on the classical systems of physics (electrons, nuclei) which are capable of being readily visualized. Thus, from this standpoint much of quantum mechanics does not really provide an entirely new way of investigating natural phenomena; in many respects quantum mechanics represents an evolution of classical mechanics which introduces wavefunctions and quantization. In this sense we can develop a "quantum" intuition that is based on classical mechanics of the world around us. The classical mechanics will be usefully employed to provide the pictures we will use to understand processes that occur in the quantum mechanical world. There will be, however, some features of quantum mechanics which could not at all be considered as an evolution of classical mechanical,

such as the consequences of electron exchange (Pauli Principle) and the indeterminacy of measuring precisely certain quantities (Uncertainty Principle).

We shall see that a wave function of the species involved in Sch. 2.1 (R, *R, I, *I, *P, P) can all be viewed as consisting of three visualizable components or separate wavefunctions: a wavefunction which describes the positions in space of the electrons (the electronic configuration), a wavefunction which describes the position of the nuclei in space (the nuclear configuration) and a wavefunction which describes the position of electron spins in space (the spin configuration). In this chapter *we shall employ electronic orbitals to visualize electronic configuration wave functions, vibrating masses connected by springs to visualize nuclear configuration wave functions, and precessing vectors to visualize electron spin configuration wave functions*. Each of these visualizations can be associated with the mathematical paradigms of quantum mechanics in a qualitative manner that will allow a useful interpretation and understanding of a wide range of photochemical phenomena.

2.2 *Molecular Wave Functions and Molecular Structure*

Conventionally a complete molecular wavefunction is composed of a complicated and abstruse mathematical function given the symbol Ψ (the Greek capital letter “psi”). Quantum mechanics provides an understanding of molecular structure, molecular energetics and molecular dynamics based on the use of molecular wave functions Ψ and on mathematical computations which use the wavefunction Ψ as a base function. According to the paradigm of quantum mechanics, *if the mathematical form of Ψ is known precisely for a given molecule, it is possible, in principle, not only to compute the electronic, nuclear and spin configurations of a molecule, but also to compute the average value of any experimental observable property (energy, dipole moment, nuclear geometry, electron spin, transition probabilities, etc.) of a given state of a molecule for an assumed set of initial conditions and interactions.*

But where do wavefunctions come from? According to the laws of quantum mechanics, a wave function Ψ produced by solving the famous Schrödinger wave equation (Eq. 2.1)

$$H\Psi = E\Psi \quad (2.1)$$

In words, Eq. 2.1 is a mathematical expression of fundamental *laws* of nature, which are considered in the same sense as Newton's laws. According to the laws of quantum mechanics, in nature the only possible stable (time independent or stable) states correspond to Ψ , the wave functions which are solutions of Eq. 2.1 and the only allowed energies are E , which are solutions of Eq. 2.1. In the wave equation H is called the "Hamiltonian" operator and corresponds to a mathematical "operator" (a mathematical procedure that changes one function into another) for the *possible energies* of the system. These energies may be the electronic energies of the molecule, the vibration energies of the molecule or the spin energies of the molecules. The special properties of Eq. 2.1 are that the "possible" or "allowed" (stable) wavefunctions, Ψ , have the remarkable property that when the mathematical operator H is multiplied by Ψ the result is E times Ψ . This extraordinary mathematical property is associated with the mechanics of stationary waves, where only certain waves or vibrations are stable and each of the stable waves has an associated energy, E . These stable waves provide a powerful analogy to the wave functions Ψ corresponding to stable states which have an energy E . In the mathematics of quantum mechanics, the energy E (in general there will be a unique energy associated with a ground state, R , excited states, $*R$ and reactive intermediates, I), a particular solution of the wave equation, is called an *eigenvalue* ("proper" value or solution in German) and the wavefunction Ψ is called an *eigenfunction*.

In the following discussion, students who are unfamiliar with the mathematics of quantum mechanics might think of the complete molecular wavefunction Ψ as a mathematical representation of the entire molecular structure, electronic, vibrational and spin. For the molecular structural representations of R , $*R$, I and P in Sch. 2.1, there exist corresponding wave functions $\Psi(R)$, $\Psi(*R)$, $\Psi(I)$, and $\Psi(P)$, respectively. A system whose wavefunction is an eigenfunction of some operator which represents a measurable property of a system is said to be in a (stable) *eigenstate* for the measured property. The explicit mathematic form of Ψ will not see the light of day in this text, but we will appeal

to pictorial representations or graphs of Ψ and we shall relate these representations the appropriate features of the familiar molecular structures.

Although the details of quantum mechanical calculations are beyond the scope of this text, it is important to know that well established computational methods exist to determine the wave functions of electron, nuclear and spin configurations of organic molecules. The student is probably familiar with "stable waves" of macroscopic objects such as vibrating springs, oscillating strings and tuning forks. These can be described in terms of wave equations for which the eigenvalues correspond to stable vibrations or oscillations.

Because of the mathematical complexity of the "true" or "exact" molecular wave function Ψ , a means of developing approximate wave functions is employed in all actual quantum mechanical computations. Fortunately, through the useful, if approximate and qualitative use of quantum mechanics, it is possible to approximate the wave function and translate it into a visualization that captures the essential features of the mathematics underlying the wave function. Within this context of approximation, a picture, especially a mathematical picture or geometry, may be a useful approximation if it contains rich intuitive information and is capable of intellectual manipulation to make predictions and direct interpretations of experimental results.

In addition to providing allowed wavefunctions Ψ to describe molecular systems and to predicting the energies E of the states associated with the allowed wavefunctions, quantum mechanics is concerned with predicting the allowed values of any molecular property of interest. For example, one might ask the following questions such as the concerning the species in Sch. 2.1:

- (1) What are the detailed electronic structure of *R and I?
- (2) What are the electron distributions of *R and I?
- (3) What is the probability of light absorption by R and the probability of light emission by *R?
- (4) What are the rates of the photochemical and photophysical transitions of *R?

Quantum mechanics provide mathematical recipes for computation of any experimentally measurable property, base on the mathematical manipulation of the wavefunction. According to the laws of quantum mechanics, all the measurable

information about a system is contained in the wavefunction Ψ . More generally than computation of the energy, E , according to quantum mechanics, each observable (measurable) property, of a system can be represented by an operator (we'll use the symbol \hat{P} for a general operator and the symbol P for the property), a mathematical procedure on the wavefunction of the system. The outcome of an observation of a particular property is calculable by performing the appropriate mathematical operation on the wavefunction Ψ (e.g., operation of the Hamiltonian operator, H , on Ψ produces the allowed energies). The operator is related to some measurable property of a system (energy, dipole moment, bond angle, angular momentum, transition probability, etc.) and generally has a form similar to the mathematics that are used to compute the classical property.

We finish this section with two important general conclusions derived from the laws of quantum mechanics:

(1) The only possible values of a measurement must be eigenvalues of equations of a form similar to Eq. 2.2. For example, in general for *every measurable property of a molecular system* there will be an operator \hat{P} which operates on Ψ to produce eigenvalues P , which correspond to an experimental measurement of that property of the system.

$$\hat{P}\Psi = P\Psi \quad (2.2)$$

(2) Eq. 2.2 refers to a single measurement in an experiment on a single molecule. A large number of experiments are actually performed on a huge number of molecules in a real experiment so that an average value of the property, P_{Ave} is obtained in a laboratory experiment. According to the laws of quantum mechanics, the average measurement, P_{Ave} is obtained by integration of the form of Eq. 2.3 (a short hand for the actual mathematics which involve complex functions and "normalization").

$$P(\text{observable property}) = \int \Psi P \Psi \quad (2.3)$$

We shall now describe the most common approximation for Ψ that is employed to solve Eq. 2.1 and thereby produce a set of allowed approximate wavefunctions and approximate energies of a system. We then will use these approximate wavefunctions to visualize the electron configurations, the nuclear configurations and spin configurations of R, *R, I and P of Sch. 2.1. Next, we will describe some how to use these approximate wavefunctions to estimate some properties of R, *R, I and P through the use of Eq. 2.3. In these cases, in addition to visualizing the approximate wavefunctions, we will need to identify and visualize the operator, P , corresponding to the property of interest and then visualize Eq. 2.3 in which the appropriate operator is mathematically “sandwiched” between the approximate wavefunction.

2.3 The Born-Oppenheimer Approximation. A Starting Point for Approximate Molecular Wavefunctions

For organic molecules, the most important method for approximating molecular wave functions was proposed and developed by Born and Oppenheimer.¹ This approximation states that since the motions of electrons in orbitals are much more rapid than nuclear vibrational motions, electronic and nuclear motions could be treated separately mathematically, in terms of approximate wave functions that describe the electronic distribution in space and the vibrating nuclei independently. This approximation greatly simplifies the solution of Eq. 2.1. The solutions of Eq. 2.1 under the Born-Oppenheimer approximation provides approximate wavefunctions and approximate energies. For singlet states, which are of main interest for organic molecules (R and P) in their ground states the net spin is zero and is not considered in the solution of Eq. 2.1. We have seen in Chapter 1, that *R and which are typically “open electronic shell species” can be either singlet states or triplet state. However, since electron "spin" motion is due to a magnetic interaction, and since magnetic and electronic interactions interact only weakly for most organic molecules, the spin motion of electrons may also be treated independently from both the motion of electrons in orbitals and the motion of nuclei in space. The Born-Oppenheimer approximation is usually made when wave functions are computed, and is generally an excellent approximation for a stable

molecular state, such as the ground state of organic molecules, that does not interact significantly with other (electronic, vibrational or spin) states. We shall see in Chapter 3 the conditions under which this approximation breaks down.

We now assume that although there is a mathematical function Ψ that represents the "true" molecular wave functions of a molecule (i.e., is an exact solution of Eq. 2.1), in practice, since it is impossible to determine Ψ exactly approximations are necessary. Thus, we need to generate an approximate " Ψ " and furthermore, we shall seek to express this approximate wavefunction in terms of *three* independent wave functions Ψ_0, χ, \mathbf{S} which are the wavefunctions for the electron configuration, the nuclear configuration and the spin configuration, respectively. The three approximate wavefunctions Ψ_0, χ, \mathbf{S} are determined by solving Eq. 2.1 under the assumptions of the Born-Oppenheimer approximation assuming a fixed nuclear configuration and no spin considerations and then solving for the approximate " Ψ " and E. The relationship between Ψ , " Ψ " and Ψ_0, χ, \mathbf{S} are given in Eq. 2.4.

$$\Psi \sim \text{"}\Psi\text{"} \sim \Psi_0 \chi \mathbf{S} \quad (2.4)$$

"true" molecular wave function	approx. molecular wave function	orbital nuclear spin
(Exact solution to Eq. 2.1)	(Solution to BO approximation)	(approximate wave functions)

The wave function Ψ_0 represents an approximate *electronic* wavefunction (the subscript zero refers to a "Zero Order" or initial working approximation) for electron position and orbital motion in space about the positively charged (positionally frozen) nuclear framework. The wave function χ represents the approximate *vibrational* wave function (which will be discussed in detail in Section 2.18) for the fixed nuclear framework. The wave function \mathbf{S} represents the approximate wave function for spin configuration (which will be discussed in detail in Section 2.21). Thus in Zero order, the "true" molecular wave function, Ψ , is approximated by " Ψ " which in turn may be approximated in terms of three separate, approximate wave functions, Ψ_0, χ, \mathbf{S} . This approximation breaks down whenever there is a significant interaction between the electrons and the vibrations (termed vibronic interactions) or between the spins and the

orbiting electrons (termed spin orbit coupling). In essence it is the Born-Oppenheimer approximation which justifies the visualization of Ψ in terms of the approximate wave functions, Ψ_0 , χ , and \mathbf{S} and which makes the Lewis structures valid. We now proceed to describe and visualize each of the three approximate wavefunctions in more detail.

First, let us consider the approximate *electronic* wave function, Ψ_0 , which we interpret in terms of a picture of electrons in orbitals about nuclei. The detailed nature of Ψ_0 will depend on the level of sophistication desired. A common approach to approximate is not to solve Eq. 2.1 for all the electrons of a molecule, but to solve for a "one electron" molecule. The wavefunctions generated by this procedure are termed "one electron orbitals", ψ_i (given the symbol lower case "psi") each of which possess an eigen value of energy, E_i . For many qualitative analyses of molecular phenomena, Ψ_0 is usefully approximated as a composite of "one electron" molecular orbitals as shown in Eq. 2.5,

$$\Psi_0 \sim \psi_1\psi_2\dots\psi_n = \prod \psi_i \quad (2.5)$$

where ψ_i is a solution of the wave equation for a "one electron" molecule. For a discussion of these approximations, the reader is referred to any one of a number of elementary texts.² A fictitious molecule possessing only one electron does not experience any electron-electron repulsions, clearly an approximation to a real molecule, but, as experience has demonstrated, is still a remarkably useful approximation. For our purposes in this text, it is only necessary to point out that the one electron wave function ψ is at the level of approximation for orbitals that is conventionally given in introductory texts or organic chemistry (the so-called Hückel orbitals). These are the familiar orbitals that the student of organic chemistry has studied and so they will provide a certain comfort level and intuitive appeal for students who are unfamiliar with quantum mechanics. On the other hand, the wave functions corresponding to nuclear (vibrational) configuration (χ) and electronic spin configuration (\mathbf{S}) are generally not covered in introductory chemistry courses and texts and therefore will be unfamiliar to the student. As a result, we will develop pictorial representations of the wave functions χ and \mathbf{S} in

detail in this chapter in order to provide the student with some “quantum intuition” concerning vibrational wavefunctions of spin wavefunctions and thereby how to visualize vibrating molecules and electron spins according to the laws of quantum mechanics..

2.4 *Important Qualitative Characteristics of the Approximate Wave Functions*

The following qualitative characteristics of the approximate molecular wave functions Ψ_0 , χ , and \mathbf{S} are of considerable general importance for an understanding to the paradigm of Sch. 2.1:

- (a) the properties of a wave function (Ψ_0 , χ , and \mathbf{S}) are not subject to direct experimental observation, but the properties of the square of the wave function (Ψ_0^2 (and Ψ_i^2), χ^2 and \mathbf{S}^2) is subject to direct experimental observation;
- (b) the square of a wave function (Ψ_0^2 (and Ψ_i^2), χ^2 and \mathbf{S}^2) relates to the *probability* of finding the electrons, nuclei, and spins, respectively, at particular points in space in a molecular structure and therefore *provide a means of pictorially representing electrons, nuclear geometries and spins as geometric structures that represent a molecule*;
- (c) the functions Ψ_0 , χ , and \mathbf{S} *may be visualized as structures in three dimensions* with respect to a given nuclear configuration;
- (d) for molecules possessing local or overall symmetry elements, Ψ_0 (and Ψ_i), χ , and \mathbf{S} will often possess useful symmetry properties that can be related to the motion and spatial position of the electrons, nuclei, and spin, which *will provide a pictorial basis for the selection rules governing transitions between states*.

In this chapter we shall be concerned with characteristics a, b and c above and we shall see how qualitative knowledge of Ψ_0 , χ , and \mathbf{S} can lead to a pictorial description of the **key electronically excited structures**, $^*R(S_1)$ and $^*R(T_1)$, in the important working paradigms of organic photochemistry (e.g., Sch. 1.3). In particular, we seek to qualitatively estimate two important equilibrium (static) properties of molecular states: (a) the various state electronic, nuclear, and spin configurations and (b) a qualitative

ranking of the energies corresponding to the various state electronic, nuclear and spin configurations. From knowledge of (a) and (b) we shall show how to readily construct energy diagrams (Sch. 1.4) which allow the energetic ranking of the important low energy states of a given molecule. In Chapter 3 we shall describe how to extend our procedure to visualize operators which correspond to forces than trigger transitions between states of a state energy diagram, all of which have a very similar nuclear configuration (photophysical processes, $*R \rightarrow R$). In chapter 6 we shall consider how to use approximate wave functions to provide a pictorial description of transitions which cause chemical changes in the nuclear configuration (primary photochemical processes, $*R \rightarrow I$ and $*R \rightarrow F \rightarrow P$).

One may ask at this point, why deal with a wave function, such as Ψ , when it is Ψ^2 that is relevant in experiments. The short answer is that it turns out to be more convenient to express the mathematical *laws* of quantum mechanics in terms Ψ rather than in terms of Ψ^2 , yet nature has decided to connect measurable properties of molecular systems to Ψ^2 rather than to Ψ .

2.5 Postulates of Quantum Mechanics. From Postulates to Molecular Structure. The Matrix Element.

As mentioned in the previous section, in this chapter we are concerned with how knowledge of an approximate wave function can lead to a qualitative estimation of two important equilibrium properties of molecular states: (a) the state energy and (b) the state electronic, nuclear and spin configurations. From knowledge of (a) and (b) we can construct state energy diagrams. The knowledge of the molecular properties shall come from pictorial representations of the wave function.

The laws of quantum mechanics are based on several postulates. These postulates and the mathematics of wave functions form the basis of quantum wave mechanics (which we shall term quantum mechanics for simplicity). One of the most important postulates of quantum mechanics is that the average value, P , of any observable molecular property (such as the energy of a state, the dipole moment of a state, the transition probability

between two states, the magnetic moment associated with an electron spin, etc.) can be evaluated mathematically in terms of a so called *matrix element* (Eq. 2.6),

Observable Property (Experiment)	$P = \langle \Psi \mathbf{P} \Psi \rangle$	Matrix Element (computation)	(2.6)
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where \mathbf{P} is a mathematical operator representing the forces or interactions operating on Ψ to produce the property, P . When the property of interest, P , is the energy, E , of the system, \mathbf{P} is symbolized by \mathbf{H} and is called the "Hamiltonian" operator or energy operator. The quantitative evaluation of matrix elements is an important procedure in theoretical chemistry, but the mathematical details of computation of matrix elements are beyond the scope of this text.

The matrix element of Eq. 2.6 may corresponds to a measurable property such as an energy or structural feature of a molecule (dipole moment, bond length, bond angle) of a molecule or some dynamic feature of a transition (e.g., photophysical or photochemical transitions of *R). For our purposes, *the matrix element is the quantum mechanical representation of an observable property of a molecular system*. Instead of computing the matrix element mathematically, we shall attempt to "qualitatively evaluate" the matrix element by devising methods to **visualize** the components of the matrix element (i.e., the wave function, Ψ and the operator, \mathbf{P}) by attributing to them concrete structural properties that can be associated with classical mechanics, which elegantly provides us with pictorial representations, and thereafter by seeking qualitative conclusions based on these admittedly oversimplified and approximate but *useful* models.

We can now use the approximate wave functions to compute matrix elements. Thus, by combining Eq. 2.4 and Eq. 2.3, the approximate value of P is given by the matrix element of Eq. 2.7.

$$P \sim \langle \Psi_0 \chi | \mathbf{P} | \Psi_0 \chi \rangle \quad (2.7)$$

In order to "understand" the factors determining the magnitude of P and to be able to qualitatively evaluate its magnitude, we need to visualize the wave functions Ψ_0 , χ , \mathbf{S} ,

and the operator \mathbf{P} and then to perform qualitative “mathematical” operations on the picture. From Eqs. 2.5 and 2.7, the approximate value of P is given by the matrix element of Eq. 2.8.

$$P \sim \langle (\Psi_1 \Psi_2 \dots \Psi_n) \chi_S / \mathbf{P} / (\Psi_1 \Psi_2 \dots \Psi_n) \chi_S \rangle \quad (2.8)$$

We term this level of approximation of P as “working” or Zeroth-Order *approximation*. By this we understand that we are within the Born-Oppenheimer approximation (separation of electronic, nuclear, and spin motion) and that we are dealing with one electron orbital wave functions (Hückel theory). In the next highest level of approximation, the so-called, First Order approximation, ***we challenge some aspect of the Zeroth-Order approximation and note its effect on the magnitude of P.*** For example, we might begin to “mix” the one electron wavefunctions. Mixing wave functions is nothing more than a mathematical process which leads to a better approximation of the wave function in First Order than we had in Zero Order. The new wave function, if the mixing is done properly, is closer to the “true” wave function, Ψ . In this approximation we only use the one electron wavefunctions that come from solution of the simple one electron molecule model. For example, we can let the electron's orbital motion mix with its magnetic spin motion (spin-orbit coupling), or we might introduce the idea of electron-electron repulsion (electron correlation or configuration interaction), or we might consider how vibrations mix electronic states (vibronic interactions), and note how the magnitude of P is influenced as a result of these "First Order Mixing" effects. If we have selected a good Zero Order approximation, the extent of mixing will be small and the mixing can be handled by “perturbation theory” which will be discussed below. If the mixing is strong, this is a signal that the Zero Order approximation is not a good one and should be replaced by a better starting point to describe the approximate wavefunctions.

In addition to making a First Order adjustment to the wave function, we may modify the operator, \mathbf{P} . For example, the Zero Order hamiltonian does not have electron-electron interactions or spin-orbit interactions included in it.

2.6 *The Spirit of the Use of Quantum Mechanical Wave Functions, Operators and Matrix Elements*

In the previous sections the wave function of a molecule, Ψ , was defined in terms of a mathematical solution of a wave equation, Eq. 2.1. The spirit of the meaning of the "true molecular wave function" Ψ is similar to the spirit of the great conservation laws (energy, momentum, charge, mass), which we assume to be correct in detail, if we knew all the details (the devil is in the details!). Similarly, *if* Ψ were known exactly and the correct operators P for all of the observable properties of a molecule were known, then according to the postulates of quantum mechanics Eq. 2.6 could be used to compute the matrix element corresponding to values of all of the observable properties of a system (state). Quite often a good level of approximation of the quantum mechanical system for qualitative studies is achieved by appealing to classical mechanics at a starting point for describing the system and then adjusting the system to include quantum effects. In these cases approximate matrix elements are computed (Eq. 2.7 and Eq. 2.8)

Classical mechanics deals with observables such as position and momentum as "functions" and postulates that all the information required to describe a **mechanical system** is available if knowledge of the "functions" describing the position and momentum of the entities that make up the system is known. Newton's laws of motion enable these "functions" to be displayed in a mathematical form.

In a similar fashion, quantum mechanics postulates that all the information about a **molecular system** is contained in its wave function Ψ , and that in order to extract the information about the value of an observable, some mathematical operation, P , must be performed on the function (Eq. 2.3). This is analogous to the necessity of doing an act (an experiment) on the system in order to make a measurement of its state. Problems in quantum mechanics often boil down to (1) selecting the proper approximation to solve for Ψ and/or (2) making the correct selection of the operator (P). Thus, the selection of the correct "operators" (mathematical operations) or interaction leading to observable properties is as crucial to the explicit solution of a problem in quantum mechanics as is knowledge of the form of Ψ .

Two of the key "operators" of quantum mechanics are related to the classical, dynamical quantities of the *momentum* and *position* of a particles (electrons, nuclei and spins) which are also critical in Newton's equations. These operators allow the determination of the energy levels of the system for the electrons, vibrations and spins. Once the operators for these dynamical variables have been selected, it usually turns out that operators for many observables can be set up in terms of these two fundamental variables. In the same manner that Zero Order wave functions are employed to approximate Ψ , in a quantitative evaluation of a *matrix element*, we almost always begin with a workable Zero Order approximate Hamiltonian or energy operator, H_0 , which is postulated to be the dominant set of interactions Ψ responsible for the energies of the electronic orbital of the molecule. In the First Order approximation we consider interactions, H_1 that are "weak" (e.g., interactions of electrons with vibration and of electrons with spins) relative to those described by H_0 but which can be important in causing transitions between the Zero Order states, especially Zero order states that are close in energy.

In the text we employ the paradigms of molecular photochemistry to identify and visualize the wave function operators which are plausible in determining the pathways of photochemical reactions. These visualizations will provide us with the "quantum tuition" that we seek to employ the power of quantum mechanics to the assist in the understanding of photochemistry. The combination of visualization of the wave functions and the interactions that operate on these wave functions will provide an intellectually gratifying and practical, if approximate, understanding of most of the important features of modern molecular organic photochemistry. Of course, we admit that there are pitfalls and risks associated with such an approach, but we will accept it as a partial, if somewhat flawed, understanding that is better than incomprehension, reminiscent of a life in wonderland.

2.7 Atomic Orbitals, Molecular Orbitals, Electronic Configuration, and Electronic States

We propose to visualize a representation of the electronic portion of “exact” wavefunction Ψ by approximating its electronic part, Ψ_0 as a structure, namely a configuration of overlapping, but non-interacting occupied one electron orbitals (Eq. 2.5). It is assumed that the reader is familiar with the manner in which a molecular orbital is approximated as a sum (or superposition) of atomic orbitals, $\Sigma\psi_i$, (e.g., Eq. 2.5).² A primary goal of this chapter is to develop a protocol for generating a state energy diagram (Sch. 1.3) for a given stable ground state nuclear geometry of an organic molecule (R) and for the low lying electronically excited states (*R) of the molecule employing one electron orbitals.

The general procedure is as follows. For a given nuclear geometry (Born-Oppenheimer approximation) of a molecule, it is assumed that appropriate one-electron (Hückel) molecular orbitals (MO)'s are filled with the available electrons to generate a set of molecular electronic configurations. Only the lowest energy configuration (ground configuration, R = S₀) and the first or second low-energy excited configuration (*R = S₂, S₁ T₁ or T₂) generally need to be considered explicitly for the overwhelming number of organic photochemical reactions. This situation corresponds to a *Zero Order molecular electronic configuration* (Born-Oppenheimer approximation, one-electron orbitals). In order to generate proper *molecular electronic states* we would have to take into account electron-correlation in some manner in the *First Order approximation which accounts in some manner for electron-electron interactions which are missing in the one electron molecule (only one electron, no electron-electron interactions!)*.

2.8 Ground and Excited Electronic Configurations

As an example of the procedure for constructing electronic configuration for the ground state, we select the formaldehyde molecule H₂CO as an *exemplar*. This exemplar captures the important features of excited state configurations of many organic molecules of photochemical interest and the lessons learned from the exemplar can be readily extended to more complicated systems. The energies of the one electron MO's for H₂CO increase in the order shown in Eq. 2.9. In Eq. 2.9 1s_O, 2s_O, and 1s_C refer to the

essentially atomic, non-bonding MO's localized on oxygen (O) and carbon (C), and the other MO's refer to conventional representations of bonding and antibonding orbitals.

$$1s_O < 1s_C < 2s_O < \sigma_{CH} < \sigma_{CO} < \pi_{C=O} < n_O < \pi_{C=O}^* < \sigma_{CO}^* < \sigma_{CH}^* \quad (2.9)$$

All of the bonding and non-bonding orbitals are filled in the ground state, S_0 . From Eq. 2.9 we note that for S_0 there exist a series of unoccupied antibonding orbitals, the lowest energy of which is the π_{CO}^* orbital. In addition, unoccupied σ_{CH}^* and σ_{CO}^* orbitals lie at very energies. The highest energy *occupied* molecular orbital in the ground state of H_2CO is the n_O orbital. This orbital is termed the HOMO (or more compactly, HO) orbital. The lowest energy *unoccupied* orbital of H_2CO is the π_{CO}^* orbital. This orbital is termed the LUMO (or more compactly, LU) orbital. We shall see that a simple and useful approximation to the process $R + h\nu \rightarrow {}^*R$ is to consider the absorption of light as resulting from a transition between molecular orbitals (such as a HOMO \rightarrow LUMO transition) that is induced by the absorption of a photon. We shall see that of all of the MOs, the HOMO and LUMO generally are of greatest importance in organic photochemistry. The HOMO and LUMO play a critical role in analyses of photochemical processes, since these two orbitals determine the lowest energy transition from R to *R . The initial photophysical and photochemical aspects start from *R , which we shall see can be characterized as having one electron in the HO and one electron in the LU. Now we address the issue of how to picture and describe the occupied orbitals in S_0 , S_1 and T_1 , the key excited states of the state energy diagram (Sch. 1.3).

What is the electronic configuration of the lowest energy electronic state of an organic molecule, S_0 , for our exemplar molecule H_2CO ? H_2CO possess 16 electrons which must be distributed to the available MOs given in Eq. 2.9. In general, the energetic order of the molecular orbitals, the number of available electrons, and the Pauli and Aufbau principles are employed to determine the ground-electronic configuration of a molecule. The ground state, S_0 , is constructed by adding electrons two at a time (Pauli Principle) to the lowest energy orbitals (Aufbau Principle) first until all of the electrons have been assigned to available orbitals. The configuration of the ground state of H_2CO

constructed according to these rules is represented by Eq. 2.10, in which the superscripts designate the number of electrons in each orbital, the label in the () designates the kind of orbital that is occupied and the subscript designates the nature of the orbital. The very σ_{CO}^* and σ_{CH}^* orbitals are omitted for simplicity, since they are of such high energy relative to the π_{CO}^* .

$$\Psi_0(\text{CH}_2=\text{O}) = (1s_0)^2(1s_{\text{C}})^2(2s_{\text{O}})^2(\sigma_{\text{CH}})^2(\sigma'_{\text{CH}})^2(\sigma_{\text{CO}})^2(\pi_{\text{CO}})^2(n_{\text{O}})^2(\pi_{\text{CO}}^*)^0 \quad (2.10)$$

The total electronic distribution of an electronic configuration may be approximated as a superposition of each of the occupied MO's that make up the configuration (Eq. 2.5). However, as in the case of writing Lewis structures, it is a useful and valid simplification to explicitly consider only the *valence electrons* when considering chemical or photochemical processes, and considering the “core” electrons as being close to the nuclei and too stable to be perturbed during chemical or photochemical processes. In a further simplification, it usually suffices to consider explicitly, only the highest energy valence electrons. In the case of $\text{CH}_2=\text{O}$, we shall consider both π_{CO} and n_{O} because they are of comparable energy and turn out to both be potential HOMOs in substituted carbonyl compounds. We shall also indicate the π_{CO}^* orbital explicitly, even though it is unoccupied in S_0 , since the π_{CO}^* orbital is clearly the LUMO for $\text{CH}_2=\text{O}$ and most carbonyl compounds. With the latter approximations in mind, a shorthand notation for the ground state electronic configuration of $\text{CH}_2=\text{O}$ is given by Eq. 2.11:

$$\Psi_0(\text{CH}_2=\text{O}) = \text{K}(\pi_{\text{C}=\text{O}})^2(n_{\text{O}})^2(\pi_{\text{C}=\text{O}}^*)^0 \quad \text{Ground state, } S_0 \quad (2.11)$$

In Eq. 2.11, K represents the “core” electrons (electrons in σ or lower energy orbitals) that are “tightly bound” to the molecular framework, i.e., are close to, and are stabilized by, the positive nuclear charge. For nearly all qualitative purposes to be discussed in this text, the electrons symbolized by K are not significantly “perturbable” during photophysical and photochemical processes. This “non-perturbability” is the basis of the validity of the approximation given by Eq. 2.11.

By an analogous protocol, if we ignore the lower energy MO's, we may describe the ground state electronic configuration of ethylene ($\text{CH}_2=\text{CH}_2$) by Eq. 2.12:

$$\Psi_0(\text{CH}_2=\text{CH}_2) = K(\pi_{\text{C}=\text{C}})^2(\pi_{\text{C}=\text{C}}^*)^0 \text{ Ground state, } S_0 \quad (2.12)$$

In the case of $\text{CH}_2=\text{CH}_2$ it is sufficient to consider only π_{CC} and $\pi_{\text{C}=\text{C}}^*$ explicitly because the electrons in the σ orbitals are of much lower energy and the σ^* orbitals are of very high energy. For $\text{CH}_2=\text{CH}_2$ the $\pi_{\text{C}=\text{C}}$ orbital is the HOMO and the $\pi_{\text{C}=\text{C}}^*$ orbital is the LUMO.

We are now in a position to describe the electronically excited states *R in terms of orbital configuration. The *lowest energy electronic states*, which are most important in organic photochemistry (see the energy diagram Sch. 1.3) possess an electronic configuration for which an electron has been removed from the HOMO of the ground state configuration and placed into the LUMO of the ground state configuration. As examples, the lowest excited states of formaldehyde and ethylene possess the following electronic configurations (Eqs. 2.13 and 2.14). The wave function for an electronically excited state Ψ^* is labeled with a $*$ (termed "star") to emphasize that the state is electronically excited.

$$\Psi^*(\text{CH}_2=\text{O}) = K(\pi_{\text{C}=\text{O}})^2(n_o)^1(\pi_{\text{C}=\text{O}}^*)^1 \quad \text{Electronically excited state, } ^*R \quad (2.13)$$

$$\Psi^*(\text{CH}_2=\text{CH}_2) = K(\pi_{\text{C}=\text{C}})^1(\pi_{\text{C}=\text{C}}^*)^1 \quad \text{Electronically excited state, } ^*R \quad (2.14)$$

The use of electron orbital configurations allows us to enumerate, to visualize, to energetically rank and to conveniently classify electronic states, *R , and to describe transitions between electronic states in electronic structural terms. For example, we expect that formaldehyde (Figure 2.1a) will have two relatively low-energy electronic transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) that will produce two corresponding electronic excited

state configurations, $*R(n,\pi^*)$ and $*R(\pi,\pi^*)$. On the other hand, ethylene will have only one low-energy electronic transition ($\pi \rightarrow \pi^*$) and one corresponding electronic excited state configuration $*R(\pi,\pi^*)$.

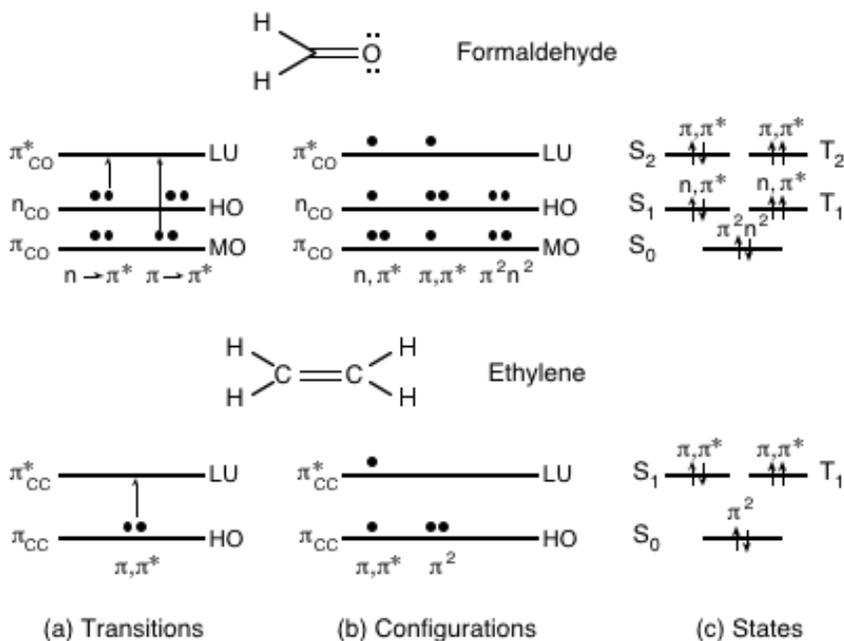


Figure 2.1 Schematic representation of (a) electronic transitions (b) electronic configurations and (c) electronic states for the lowest excited states of formaldehyde (top) and ethylene (bottom). The arrows for the states refer to the relative orientation of the two electrons in the HO and LU.

In the above discussion we have developed an abbreviation Scheme for describing orbitals and states that shall be employed throughout the text and which is widely employed in the photochemical literature. In general, we shall describe ground configuration of molecules in terms of the highest energy filled MO, or when appropriate and useful, in terms of the two highest energy filled MO's. Electronically excited configurations shall be described in terms of the two singly occupied MO's, usually the HOMO orbital and the LUMO orbital (e.g., n,π^* and π,π^*). Transitions shall be described only in terms of the orbitals undergoing a change in electronic occupancy (e.g., $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$). This very handy short hand notation for electron configurations also provides a useful method to represent excited *states*, such as S_1 and T_1 as we shall show in the following Sections.

2.9 *The Construction of Electronic States from Electronic Configurations*

The goal of this chapter was the development of ideas of molecular structure to enumerate, classify, energetically rank and qualitatively visualize the electronic, vibrational and spin nature of molecular states that appear in the state energy diagram of an organic molecule (Sch. 1.4). We now make an important distinction between the structure of singlet and triplet states that may be derived from the same electronic orbital and nuclear geometric configuration when the same two orbitals are half-occupied, i.e., n, π^* and π, π^* configurations. The structural difference for the same orbital occupancy for a given nuclear configuration resides in differences in the configuration of the spins of the electrons in the two half filled orbitals and the operation of the Pauli principle.

2.10 *Construction of Singlet and Triplet States from Electronically Excited Configurations and the Pauli Principle*³

The Pauli principle demands that any ground state configuration (such as that for formaldehyde in which the electrons are all paired in orbitals) must be a ground state *singlet* (in Section 2.26 we shall discuss the origin of the terms singlet and triplet), i.e., the spins of the two electrons which occupy a single orbital must be paired. In the excited state two electrons are *orbitally unpaired*, i.e., each electron is in a different orbital, one in a HOMO and the other in a LUMO. The Pauli principle allows, but does not require, the spins of two electrons to be paired, if they do not occupy the same orbital. As a result, *either* a singlet excited state in which there is no net spin (i.e., the two electrons which are orbitally unpaired (HOMO and LUMO singly occupied) and electron spins are antiparallel ($\uparrow\downarrow$) or paired as in the ground state) or a triplet excited state (the two electrons which are orbitally unpaired (HOMO and LUMO singly occupied) and the electron spins are parallel ($\uparrow\uparrow$) or unpaired) may result from the same electronic configuration of two electrons in half-occupied orbitals. This means that each of the **same** excited electronic configurations given in Figure 2.1b can refer to either a singlet (S) or to a triplet (T) electronic *state*.

Thus, *four states, two singlets and two triplets* result from the *two lowest energy* electronic excited electronic configurations of formaldehyde. The lower energy n, π^*

state may be either a singlet (S_1) or a triplet (T_1) configuration, and similarly the higher energy π, π^* state may be either a singlet (S_2) or triplet (T_2) configuration. These states are displayed in Fig. 2.1c (See a more detailed description of the orbital configuration and spin occupancy in Fig. 2.2).

2.11 *Characteristic Configurations of Singlet and Triplet States: A Shorthand Notation*

The conventions described in Chapter 1 for the state energy diagram of a molecule (Sch. 1.4) serve as a basis for a convenient notation to describe electronic configurations and electronic states. We term the ground (lowest energy) electronic singlet state S_0 , where S indicates there is no net electronic spin associated with the state (i.e., each spin up is matched by a spin down, $\uparrow\downarrow$) and the subscript zero refers to the *ground electronic state*. We reserve the subscript zero for the ground electronic ground state S_0 . Therefore, for triplet states with parallel spin ($\uparrow\uparrow$) we label the *first* triplet level located energetically above S_0 as T_1 , where T indicates a *threefold* degeneracy of the state (in a magnetic field) due to the three possible alignments of two unpaired spins (to be discussed below in Section 2.27) and the subscript 1 refers to the energy ranking among triplet states relative to S_0 .

We label electronically *excited singlet* states S_1, S_2 , etc., where the subscript refers to the *energy ranking* of the state relative to the ground state (arbitrarily given the rank of energy equal to zero and all other states possessing positive energy relative to the ground state). Thus, S_1 is the *first* electronically excited *singlet* state located energetically above S_0 , and S_2 is the *second* electronically excited *singlet* state located energetically above S_0 . Similarly, T_1 is the *first* electronic *triplet* state located above S_0 and T_2 is the *second* electronic *triplet* state above S_0 .

As a shorthand, we describe electronic and spin *configurations* in terms of the key molecular *orbitals* that are expected to dominate the energy and/or chemistry of the configuration. Thus, for formaldehyde we need to explicitly consider only the $\pi_{C=O}$, n_O , and $\pi^*_{C=O}$ orbitals in discussing electronic configurations, and hence in discussing

electronic states, in a state energy diagram. This approximation assumes that consideration of the lower lying σ orbital and the higher energy σ^* orbital is not necessary for an understanding of the photochemistry of formaldehyde. As a result of the above discussion we may state the following rule: Each electronic state may be described (a) in terms of a *characteristic electronic configuration*, which in turn may be often be described in terms of the HOMO and LUMO orbitals: (b) in terms of a characteristic spin configuration, either singlet ($\uparrow\downarrow$) or triplet ($\uparrow\uparrow$).

In summary, the use of electronic and spin configurations to describe the S_0 , S_1 , S_2 , T_1 and T_2 states of formaldehyde may be described as shown in Table 1. In addition based on the individual orbital energies, we can rank the energy of the n,π^* state of a given spin as unambiguously being lower in energy than the corresponding π,π^* states of the same spin, e.g., $S_1(n,\pi^*)$

Table 1. States, characteristic orbitals, characteristic spin configurations and shorthand description of low lying states of formaldehyde.

State	Characteristic Orbitals	Characteristic Spin Electronic Configuration	Shorthand Description of State
S_2	π,π^*	$(\pi)^1(n)^2(\pi^*)^1$	$1(\pi,\pi^*)$
T_2	π,π^*	$(\pi)^1(n)^2(\pi^*)^1$	$3(\pi,\pi^*)$
S_1	n,π^*	$(\pi)^2(n)^1(\pi^*)^1$	$1(n,\pi^*)$
T_1	n,π^*	$(\pi)^2(n)^1(\pi^*)^1$	$3(n,\pi^*)$

S₀

π, n

$(\pi)^2(n)^2$

$\pi^2 n^2$

In many cases a single electron *configuration* is adequate to approximate the electronic characteristics of an electronic *state*. In some cases, however, a combination of two or more electronic configurations will be required to achieve a good approximation of a state. This is the situation when two states in Zero Order have similar energy and can be coupled by some interaction, say a vibrational motion. In this case, we say the a single electron orbital are inadequate as a description because these orbitals are "mixed", i.e., an n orbital may mix in some π character as the result of a vibration (Section 3.6). We shall see examples of "mixed" n, π^* and π, π^* states, where neither "pure" configuration provides an adequate representation of the actual state, but the "mixed" or "First Order" representation works well. Perturbation theory teaches the rules for such mixing and will be discussed in Chapter 3.

2.12 Electronic Energy Difference between Singlet and Triplet States

The student may recall from General Chemistry Hund's rule, which states that for atoms a triplet state that is derived from a given electronic configuration possessing two half-filled orbitals is *always* of lower energy than the corresponding singlet state derived from the *same* configuration, i.e., $^1E(n, \pi^*) > ^3E(n, \pi^*)$ and $^1E(\pi, \pi^*) > ^3E(\pi, \pi^*)$. A physical and theoretical basis for Hund's rule is available from consideration of the implications of the Pauli principle. The Pauli principle operates as a sort of quantum mechanical "traffic cop for electron motion" which "instructs" the two key orbitally unpaired electrons in triplet states how to "avoid" one another. The Pauli principle requires the electrons to *correlate* their motions because two electrons of the same spin are absolutely not allowed to occupy the same space at the same time. The electrons in a singlet state are not compelled to obey the Pauli principle and may on occasion approach the same region of space. This will always serve to raise the energy of the singlet state relative to the triplet. Thus, by being instructed to avoid being in the same place,

electrons in a triplet state are able to minimize electron-electron repulsions relative to a singlet state in which the electrons are allowed to approach without the Pauli restriction.

Thus, the difference in *electronic energy*, ΔE_{ST} , between singlet and triplet states (that are derived from the same electron orbital configuration) results from the "better" correlation of electron motions in a triplet state producing lower electron-electron repulsions. Although Hund's Rule strictly speaking refers to the states of atoms, it may be applied to molecules also. In order to visualize how this singlet-triplet energy separation (ΔE_{ST}) arises for a given orbital configuration of a molecule and to gain an appreciation of how the magnitude of the ΔE_{ST} depends upon the orbitals comprising the characteristic configuration, we attempt to visualize the magnitude of *matrix elements* that evaluate the electronic energy of orbitals, configurations.

2.13 Evaluation of the Singlet-Triplet Energy Gap for Electronic States of the Same Configuration

A state energy is the summation of all of the Zero Order energies (one-electron orbital, no electron-electron interactions) plus electron-electron repulsion energies in First Order. In the Born-Oppenheimer approximation, the nuclear geometry is fixed and the attractive forces between the negative electrons and the fixed positive nuclear framework are assumed to contribute a certain stabilization energy. The differences in energy between different states in this approximation is due entirely to electron-electron repulsions. Thus, when we discuss electronic energy differences between two states we are referring to the differences between electron-electron repulsions in the two states. The state with the smaller electron-electron repulsions has the lower energy. The classical operator for the energy increase due to electron-electron repulsions is defined by the familiar *electrostatic* or Coulombic repulsion between electrons, i.e., e^2/r_{12} where e is the charge of an electron and r_{12} is the separation between the electrons. The Coulombic interactions between two electronic distributions is always repulsive and the value of this electronic repulsion may be computed by integration of the repulsive interactions over all of the volume of a molecule assuming a fixed positive molecular framework (Born-Oppenheimer approximation). The matrix element for the *total* electron-electron

repulsion energies are broken down into two types: (1) the repulsions between electrons due to *classical mechanical electrostatic interactions* (termed Coulombic interactions and given the symbol K) and (2) the repulsions between electrons when *quantum mechanical interactions due to the Pauli Principle* (termed electron exchange interactions and given the symbol J) *are taken into account*. J is referred to as the electron ***exchange integral*** because the Pauli Principle is derived from a postulate on the symmetry property of electrons when two electrons exchange positions in space with one another. The exchange integral is a purely quantum mechanism phenomena and amounts to a quantum mechanical correction to the classical electronic distribution which does not take into account the influence of electron spin on electron-electron correlation and therefore electron-electron repulsion. Quantum intuition comes from the acceptance of the Pauli Principle as follows. When the nuclei of two atoms come close enough together (ca 3 Å or less) the wavefunctions (electron clouds) of the two atoms begin to overlap slightly. Although the individual wavefunctions may not be significantly perturbed as they approach, when even a small amount of overlap occurs, the electron from one atom will have an unavoidable tendency to slip from the nucleus of its atom and visit the nucleus of the other atom. This intuition when coupled with that Pauli concept that quantum spin correlation which causes electrons of the opposite spin ($\uparrow\downarrow$) to have an enhanced probability of being found near one another (in spite of the added repulsions that proximity brings) and simultaneously causes electron of the same spin ($\uparrow\uparrow$) to stay apart (and possess a lower energy than expected from classical considerations).

As an exemplar let us consider the energies, E, of the ground state and the lowest excited S₁ and T₁ states of formaldehyde based on the energies of the n and π* orbitals (Fig. 2.1). The energies of S₀, S₁ and T₁ are defined by Eqs. 2.15, 2.16 and 2.17, respectively.

$$E(S_0) = 0 \quad \text{by definition} \quad (2.15)$$

$$E(S_1) = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*) \quad (2.16)$$

$$E(T_1) = E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*) \quad (2.17)$$

In Eqs. 2.15 and 2.16 $E_0(n,\pi^*)$ is the Zero Order energy of the one electron excited state, $K(n,\pi^*)$ is the First Order Coulombic correction due to classical electron-electron correlation and $J(n,\pi^*)$ is the First Order quantum mechanical correction due to the Pauli Principle. Since the charges are the same for electron-electron electrostatic interactions which lead to repulsions, the values of both of the energy integrals K and J in eqs. 2.12 and 2.13 are defined as mathematically positive (corresponding to repulsions). The energy of the Coulomb integral $K(n,\pi^*)$ corresponds to the contribution of the classical charge interactions of electrons (for a fixed framework of positive nuclei) to the total energy of the molecule. As mentioned above, since the energy computed is that for the Coulombic interactions between electrons and therefore between the same charges, the value of $K(n,\pi^*)$ is always positive, corresponding to an energy increasing repulsive interaction between electrons.

The exchange energy, $J(n,\pi^*)$, is the correction that must be made to the computation of the total electronic energy of a molecular to take into account the effects of the Pauli Principle, which requires a correlation of electrons which depends on the orientation of their spins. A simple picture of the Pauli Principle is that quantum mechanics requires electrons of the same spin ($\uparrow\uparrow$) avoid approaching one another, but that electrons of opposite spin ($\uparrow\downarrow$) actually have an enhanced probability of being found near one another. Thus, we build up the quantum mechanical “intuition” that if two electrons have the same spin, the average repulsion energy will be less than the repulsion computed from the classical model because of the tendency of electrons with parallel spins to avoid each other; on the other hand, if two electrons have the same spin, the average repulsion energy between them will be greater than the repulsion computed from the classical model because of the tendency of two electrons of the same spin to couple to one another. As a result, for the T_1 state, the average repulsive energy is reduced from the expected value for the classical case, i.e., $E(T_1) = E_0(n,\pi^*) + K(n,\pi^*)$, to a lower value $E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)$. We obtain the following “quantum intuition” from the above discussion. The average repulsions between electrons are different for the same orbital configuration for singlets and triplets because when electrons have the same spin orientation ($\uparrow\downarrow$) they tend to “stick together” and suffer energy increasing repulsive

interactions, whereas in the electrons have opposite spin orientation ($\uparrow\uparrow$) then inherently avoid each other. Thus, for the same electronic configuration, the average energy due to electron repulsions for a triplet state, T_1 will always be lower than the energy of electron repulsions for the corresponding singlet state, S_1 of the same electron configuration.

Let us now estimate the difference in energy between a singlet and triplet state of the same electronic configuration. Starting with the Zero Order approximation (one electron orbitals) for a n,π^* state, let $E_0(n,\pi^*)$ be the matrix element for the Zero Order one electron orbital energy. In this case the electrons are assumed not to interact, so that the singlet and triplet energies would be identical, i.e., J and $K = 0$). Let the matrix element $J(n,\pi^*)$ be the value of the electron repulsion when the electron exchange is taken into account, and let $K(n,\pi^*)$ be the matrix element that measures ordinary classical electron repulsion due to Coulombic interactions between electrons. We can obtain ΔE_{ST} , the energy difference between $S_1(n,\pi^*)$ and $T_1(n,\pi^*)$ by subtraction of Eq. 2.17 from 2.16 to achieve Eq. 2.18, and that the values of $E_0(n,\pi^*)$ and $K(n,\pi^*)$ drops out of the evaluation so that ΔE_{ST} only depends on the value of $2J(n,\pi^*)$!

$$\Delta E_{ST} = E(S_1) - E(T_1) = 2J(n,\pi^*) > 0 \quad (2.18)$$

Since $J(n,\pi^*)$ corresponds to electron-electron repulsion and must correspond to a positive (repulsive) energy we conclude, within this approximation, that $E(S_1) > E(T_1)$ *in general* for all n,π^* states! In addition, the value of ΔE_{ST} is precisely equal to $2J(n,\pi^*)$, i.e., the energy gap between the singlet and triplet equals twice the value of the electron exchange energy. Since the details of the orbital were not considered in making the argument, we conclude that for a π,π^* electronic configuration, $S(\pi,\pi^*)$ and $T(\pi,\pi^*)$, $\Delta E_{ST} = 2J(\pi,\pi^*)$. This qualitative result can be generalized to the following conclusion: the energy gap between a singlet state and a triplet state of the same configuration is purely the result of electron exchange. It follows therefore that we can estimate the value of ΔE_{ST} if we can estimate the value of J . Let us now seek to answer the question, which is larger, in general, $\Delta E_{ST}(n,\pi^*)$ or $\Delta E_{ST}(\pi,\pi^*)$? We shall answer this question by using a pictorial approach.

2.14 An Exemplar for the of Singlet-Triplet Splittings⁹

We now consider our first pictorial representation of electronic orbitals as a means of qualitatively evaluating the value of a matrix element, namely the matrix elements for the values of energy differences $\Delta E_{ST}(n,\pi^*)$ and $\Delta E_{ST}(\pi,\pi^*)$.⁹ The estimation of ΔE_{ST} requires the estimation of the matrix elements, $J(n,\pi^*)$ and $J(\pi,\pi^*)$, the electron exchange integral (Eqs. 2.16 and 2.17). We shall consider as a specific exemplar, the (n,π^*) and (π,π^*) states of ketones. The important photophysics of ketones is described in Chapters 4 and 5 and the photochemistry of ketones is described in Chapter 9. The lowest S_1 and T_1 states of many ketones are n,π^* states, with the $S_2(\pi,\pi^*)$ and $T_2(\pi,\pi^*)$ being somewhat higher in energy, as is the case shown in Fig. 2.1. The value of $J(n,\pi^*)$ represents the electrostatic repulsion, due to electron exchange, between an electron in an n orbital and an electron in a π^* orbital.

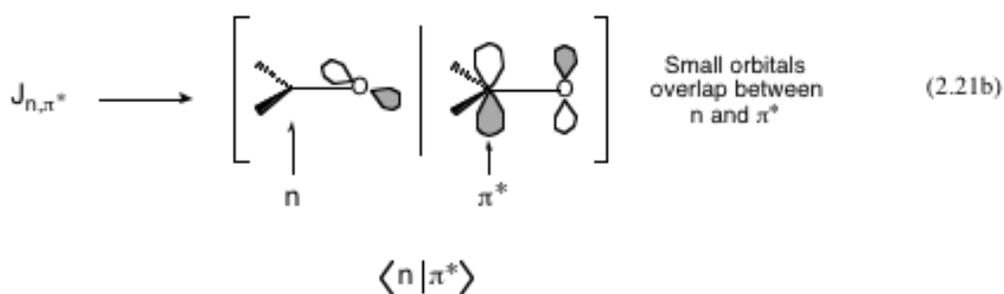
The magnitude of $J(n,\pi^*)$ is given by a matrix element shown in Eq. 2.19, in which n and π^* represent the wavefunctions for the n and π^* orbitals, respectively. The numbers refer to the electrons occupying these orbitals and e^2/r_{12} is the operator (e is the charge on an electron and r_{12} is the distance of separation between electrons) which represents the repulsion between the exchanging electrons. The latter term may be factored out of Eq. 2.19 so that the value of $J(n,\pi^*)$ can be seen to be proportional (Eq. 2.20) to the mathematical overlap of the wave functions of the n orbital with the wave function of the π^* orbital. The magnitude of this orbital overlap is represented by the symbol $\langle n|\pi^*\rangle$, termed an *overlap integral*.

$$J(n,\pi^*) = \langle n(1)\pi^*(2)|e^2/r_{12}|n(2)\pi^*(1)\rangle \quad (2.19)$$

or

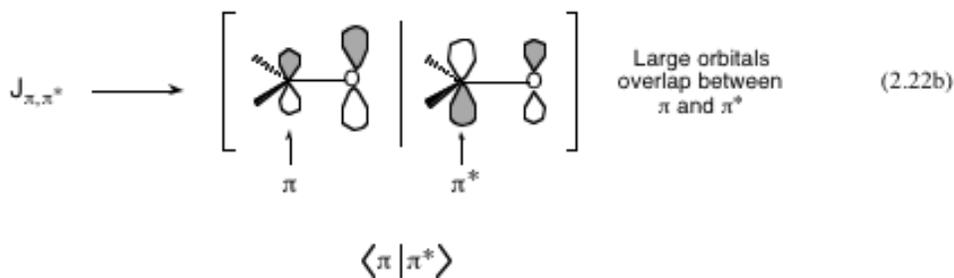
$$J(n,\pi^*) \sim e^2/r_{12}\langle n(1)\pi^*(2)|n(2)\pi^*(1)\rangle \sim \langle n|\pi^*\rangle \quad (2.20)$$

In other words, the magnitude of $J(n,\pi^*)$ will be proportional (Eq. 2.20) to the value of integral $\langle n|\pi^*\rangle$. The value of this integral is proportional to the degree of overlap of the n and π^* orbitals which we can estimate qualitatively pictorially. An overlap integral, such as that of Eq. 2.20, may be pictured as a measure of the mutual resemblance of two wavefunctions. If the two wavefunctions are identical, then the normalized value of the overlap integral, $\langle 1|1\rangle = 1$. On the other hand, if the two wavefunctions do not overlap at all then the normalized value of $\langle 1|0\rangle = 0$. We may visualize the overlap integral $\langle n|\pi^*\rangle$ if we replace the symbol n (which represents the wavefunction of the n orbital of formaldehyde) with a picture of the n -orbital and the symbol π^* (which represents the wavefunction of the non-bonding n_O orbital of a ketone) with a picture of the $\pi_{C=O}^*$ orbital (Eq. 2.21) and we picture the common regions of overlap of these orbital in the space about the nuclei of formaldehyde. We then qualitatively estimate the degree of overlap between the n and π^* orbital. We note that the overlap integral must be “small” because these orbitals do not occupy very much of the same region of space. By inspection an electron in the π^* orbital has its density above and below the plane of the molecule (assuming a planar structure). The lobe of the π^* orbital on the carbon atom does not overlap at all with the n orbital (Eq. 2.21b). Furthermore, the n orbital is in the nodal plane of the π^* which means that at this level of approximation there is exact canceling and zero overlap of the two orbitals!



Now let us compare this result to the overlap of orbitals for a π,π^* configuration. Employing the ideas leading to Eqs. 2.19 and 2.20 we obtain for a π,π^* configuration Eqs. 2.22a and 2.22b.

$$J_{\pi,\pi^*} \sim \langle \pi|\pi^*\rangle \quad (2.22a)$$

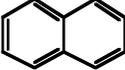
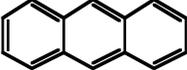


From a comparison of the orbitals we see that in this case there is significant overlap at both the C and the O atoms. It is clear that J_{π,π^*} will be greater, *in general*, than J_{n,π^*} because the overlap integral $\langle \pi | \pi^* \rangle$ will generally be greater than the overlap integral $\langle n | \pi^* \rangle$.

We can now use a physical interpretation of the overlap integrals to understand and compare the magnitude of the singlet triplet gaps for n,π^* and π,π^* states. The overlap integrals of Eqs. 2.21 and 2.22 are measures of the region of space that is common to two orbitals. If the value of the overlap integral is large then the region of space occupied by the electrons in each orbital is large and the electron-electron repulsion is large. If the value of the overlap integral is small, then the region of space occupied by the electrons in each orbital is small and the electron-electron repulsion is small. The energy “advantage” that that Pauli principle provides is that the triplet decreases as the space available for electron repulsions decreases (as the e^2/r_{12} term in Eq. 2.19 decreases and the orbital overlap decreases). From the above pictorial arguments we conclude that *in general* $\Delta E_{ST}(n,\pi^*) < \Delta E_{ST}(\pi,\pi^*)$ because the overlap of a π with a π^* orbital will in general be greater than the overlap of a n and π^* orbital.

Now we need to challenge this qualitative pictorial conclusion with some quantitative data to see if it is valid. Experimentally, values of $\Delta E_{ST}(n,\pi^*)$ states for ketones are 7-10 kcal/mole, while values of $\Delta E_{ST}(\pi,\pi^*)$ states for aromatic hydrocarbons are of the order of 30-40 kcal/mole. Table 2.2 lists some experimental values of ΔE_{ST} and shows that indeed states derived from n,π^* configurations consistently have smaller singlet-triplet splitting energies than states derived from π,π^* configurations.

Table 2.2. Some Examples of Singlet-Triplet Splittings

Molecule	Configuration S_1 and T_1	ΔE_{ST} (kcal/mole)
$\text{CH}_2=\text{CH}_2$	π, π^*	70
	π, π^*	40
	π, π^*	35
	π, π^*	35
$\text{CH}_2=\text{O}$	n, π^*	10
$(\text{CH}_3)_2\text{C}=\text{O}$	n, π^*	7
$\text{Ph}_2\text{C}=\text{O}$	n, π^*	7

The *state energy level diagram* for formaldehyde (Figure 2.1 c) may now be modified to include the singlet triplet splittings (Figure 2.2). From this point on, state energy level diagrams will be presented at least at this level of approximation.

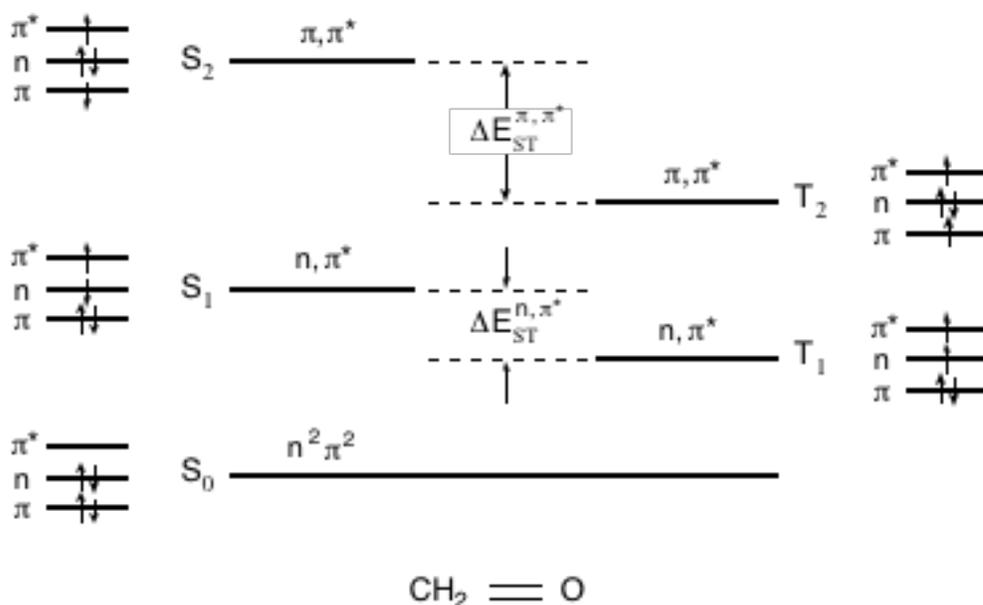


Figure 2.2 State energy diagram for formaldehyde including singlet-triplet splittings and electronic configurations of states.

2.15 Summary

The solutions of the Schrodinger wave equation (Eq. 2.1) provide the mathematical form of the wavefunctions (Ψ) of a system. Through the wavefunction, the chemist has access to computation of all the measurable properties (\mathbf{P}) of a system through Eq. 2.3 and the matrix elements corresponding to Eq. 2.6. The electron distribution of organic molecules can be described in terms of wavefunctions representing electronic configurations composed of one electron orbitals, ψ_i . This approximate description provides a qualitative framework for not only visualizing the distribution of electrons in space, but also as a means of estimating the magnitude of matrix elements for important quantities such as singlet-triplet energy gaps. We shall rely heavily on the one electron orbital model in this text and show that it is useful not only in visualizing and evaluating “static” properties such as the electron distributions, but also in visualizing and evaluating “dynamic” properties such as the probabilities of transitions between electronic states (Chapter 3).

2.16 *Vibrational Wavefunctions. The Classical Harmonic Oscillator*

We have developed one electron wave functions (ψ), and configurations of one electron orbitals ($\Pi\psi_i$) as models for approximation and visualization of the electron orbital portion of the approximate wave function Ψ_0 . Now we consider how to approximate and visualize χ , the wavefunction of the vibrational portion of Ψ_0 . Chemists are accustomed to considering vibrations in terms of nuclei oscillating back and forth in the potential field of the electrons (the Born-Oppenheimer approximation) and executing motions approximated by those of a **classical harmonic oscillator**. The classical harmonic oscillator is, therefore, a useful starting point for visualizing χ . Following the classical interpretation of the harmonic oscillator, the relationship of the classical oscillator system to the quantum oscillator will be developed.

A few comments concerning the basic features of the harmonic oscillator are in order. It is important to recognize that at the quantum level of the photon and the molecule, many important quantum systems can be approximated as vibrating harmonic oscillators: i.e., the vibrations of the electromagnetic field, the orbital motion of an electron about a nucleus, the vibrations between two atoms of a chemical bond and the precession of an electron spin about a coupling magnetic field. The importance of the harmonic oscillator is found in the fact that *the same mathematics can be employed to treat an initial, approximate description of many physically distinct systems, all of which respond to a distorting or perturbing force in the same way*. In a sense when we use the mathematics of harmonic motion we are discussing all these problems at once, even as we focus on one selected exemplar.

A harmonic oscillator may be defined as any system that, when perturbed from its equilibrium, experiences a restoring force, F , that is proportional to the displacement from its equilibrium position, r_e , Eq.2.23,

$$F = -kr, \quad (2.23)$$

where r is the distance of displacement from equilibrium, F is the restoring force and k is termed the proportionality constant related the force to the extent of displacement. The

proportionality constant k is termed the force constant for oscillation. A harmonic oscillator at rest may be set into oscillation by some impulse or perturbation that is applied suddenly. The perturbation sets the system into “harmonic oscillations”. An oscillating pendulum or a vibrating string of a violin or an oscillating tuning fork are common examples of harmonic oscillators.

When Eq. 2.23 is applicable to a system of interest, from classical physics the potential energy (the derivative of the force as a function of r) of the system can be related to the displacement r by Eq. 2.24

$$PE = 1/2kr^2 \quad (2.24)$$

The most common vibrations of an organic molecule may be classified as stretching vibrations between two bound atoms (e.g., C-H or C=O stretching) or bending vibrations between three bound atoms (e.g. H-C-H or H-C-C bending). Essentially all of the important features of the harmonic oscillator model for vibrations are incorporated into the characteristics of the stretching motion of a diatomic molecule (to only vibration available for such systems). Thus, we shall analyze a generalized diatomic molecule and apply the general results for all vibrations of an organic molecule.

The harmonic oscillator (Eq. 2.24) is often a good approximation of a vibrating system when small displacement from equilibrium positions of the atoms are considered. Let us consider a vibrating (oscillating) diatomic molecule, X-Y. For a classical harmonic oscillator, the relative vibrational motion of X with respect to Y is a periodic, oscillating function of time. The frequency, ν , of oscillation follows Eq. 2.25, where k is the same force constant (Eq. 2.23) of the chemical bond between the atoms X and Y and m is the reduced mass of the two atoms forming the bond. The significant characteristics of a classic harmonic oscillator are: (1) the amplitude (displacement) of vibration increases with the total energy of the oscillator; (2) the frequency of vibration, ν , is determined only by the mass, m , and force constant, k , and not by the amplitude of the motion; (3) the larger the force constant, k , for a given pair of masses of reduced mass m , the higher the frequency, ν ; (4) the smaller the reduced mass, m , for a given force constant, k , the higher the frequency, ν .

$$\nu = (k/m)^{1/2} \quad (2.25)$$

According to Eq. 2.24, a plot of the potential energy (PE) of a vibrating diatomic molecule as a function of internuclear separation, r , is given by the familiar *classical parabolic potential-energy* curve (Fig. 2.3). At some particular internuclear separation r_e the potential energy of the system is at a minimum, i.e., at the separation r_e the nuclei possess their equilibrium configuration. If the separation is decreased to a value less than r_e (to the left in the curves of Fig. 2.3) the potential energy of the system increases rapidly as a result of internuclear and electronic repulsions. On the other hand, if the internuclear separation is increased to a value greater than r_e (to the right in the curves of Fig. 2.3) the potential energy also increases due to the stretching of the X-Y bond. At the equilibrium position, r_e , there is no net restoring force operating on the atoms, but at any displacement from r_e , a restoring force, F in Eq. 2.23 exists. The restoring force thus varies in *magnitude* and in *direction* in a periodic fashion at frequency ν in equal intervals of times called periods, τ . We see that a pair of atoms undergoing classical harmonic motion stretch and contract back and forth through a point of separation r_e at which the potential energy, PE, of the system is a minimum. Since we will generally be interested in energy differences between vibrational levels, we may arbitrarily define the potential energy minimum as E_0 , with E_0 defined as the zero of energy and all other vibrational energies being positive (higher energy, less stable) relative to this value.

These features lead immediately to conclusions such as the expectation (1) that C-H bonds will tend to be of high frequency, because they possess large force constants (strong bonds, like a stiff spring holding the atoms together) and possess a small reduced mass (H is the lightest atom) and (2) that weak bonds between two heavy atoms such as a C-Cl bond will be of very low frequency because they possess small force constants (weak bonds, like a soft spring holding the two atoms together) and also possess large reduced mass. Fig. 2.3 left shows an example of the shape of the potential curve of a vibrating C-H bond and Fig. 2.3 right shows an example of the shape of the potential curve for a C-Cl bond. The harmonic oscillator provides powerful “quantum insights” to the properties of vibrating atoms. The stretching frequencies of C-H bonds which combine a strong bond and a small reduced mass are of the order of $\nu \sim 10^{14} \text{ s}^{-1}$.

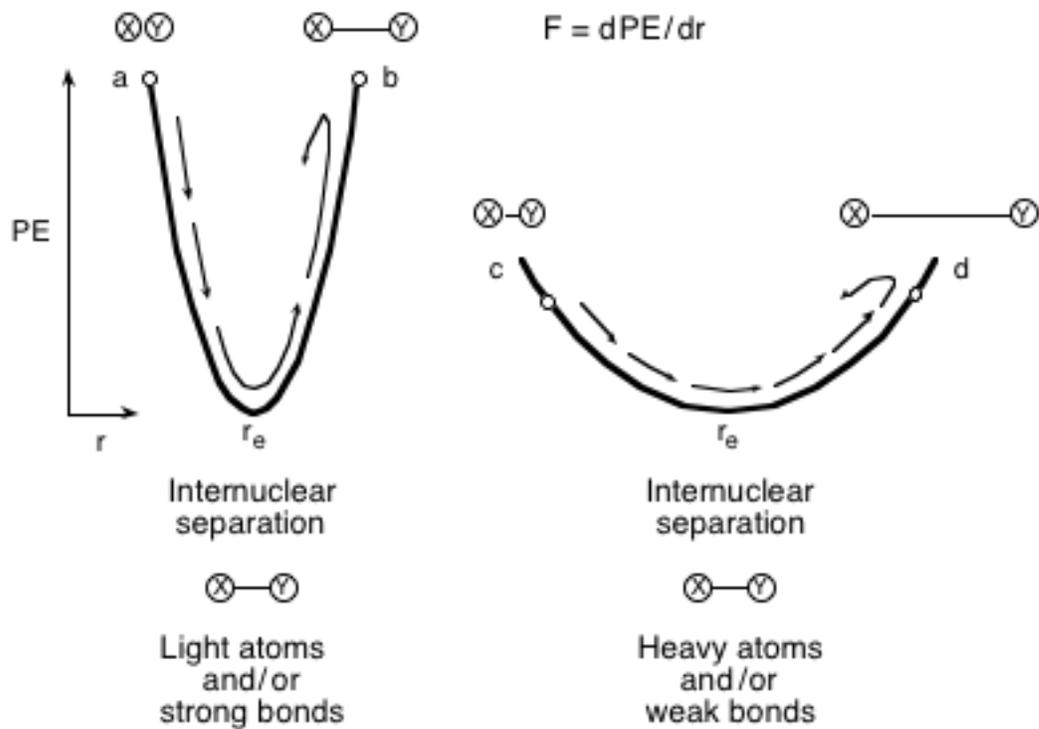


Figure 2.3. Potential energy curves for a classical diatomic molecule. Left: a diatomic molecule with a strong bond and/or light atoms. Right: a diatomic molecule with a weak bond and/or heavy atoms.

$$V = (1/2)k(\Delta r)^2 \quad (2.21)$$

At any point on the potential-energy curves of Figure 2.3, the vibrating atoms experience a restoring force F , attracting the system towards the equilibrium geometry, r_e . The magnitude of this force, F , is given by $F = dPE/dr$, i.e., the force is the ratio of the

magnitude of the potential energy of the system at any point to the displacement from equilibrium $\Delta r = |r - r_e|$. The value of the slope is a measure of the resistance of the system to distortion from the equilibrium position. From Eq. 2.24 we see that for a strong bond (large k) a large change in potential energy, PE, will occur with only a small displacement because PE is a quadratic function of the displacement. A strong bond thus corresponds to a potential curve with "steep" walls (Figure 2.3 left), such that even small displacements cause a large increase in the potential energy. A weak bond corresponds to a potential energy curve with "shallow" walls (Figure 2.3 right), such that small displacements cause a large increase in potential energy. Since the frequency of vibration, ν , is directly proportional to the bond strength and inversely proportional to the mass, a steep potential curve implies a higher frequency vibration and a shallow potential curve implies a lower frequency vibration. Thus, we expect the potential energy curve on the left of Figure 2.3 to be characteristic of a strong bond and the potential energy curve on the right of Figure 2.3 to be characteristic of weak bonds, if we compare similar reduced masses.

The term "representative point" on a potential energy curve may now be defined. We refer to a particular point on the curves of Figure 2.3 as a "representative point" corresponding to a specific displacement, Δr , on the x-axis, and which "follows" the motion (kinetic energy, KE), displacement from the equilibrium separation (Δr), and potential energy (PE) of the pair of atoms XY. For example, when the representative point, r , is at r_e , the molecule possesses zero PE (by definition). It may or may not possess KE at this position. For any other value of r on the PE curve, the molecule possesses excess potential energy. The molecular structures corresponding to such points are kinetically unstable, i.e., they are attracted toward r_e by restoring forces, just as a classical particle on a downward-sloping surface is attracted toward a potential energy minimum. Therefore, we expect any representative point at a position r to move *spontaneously* toward r_e .

Consider the points a, b Fig. 2.3 left and c, d Fig. 2.3 right which correspond to an excess of vibrational energy of the system and are the "turning points" of vibration. Suppose the representative point is initially at the turning point, a (Fig. 2.3 left), in its motion. The point will spontaneously be attracted to the equilibrium position because of

the restoring force operating on it. In moving towards r_e the system picks up kinetic energy. The total vibrational energy (E_v) of the system equals (Eq. 2.26) the potential energy (PE) + the kinetic energy (KE). The latter is maximal when the point is at r_e where the PE is zero. On the other hand, at the turning point, the KE is zero so that the total energy is equal to the PE of the system. In the absence of friction, we can visualize the representative point as oscillating back and forth between a and b. This oscillation is represented by the arrows on the curves. Similar concepts apply for oscillations between c and d. The latter occur at a lower frequency than those between a and b.

$$E_v = PE + KE \quad (2.26)$$

In summary, the classical motion of vibration of X relative to Y in a diatomic molecule may be visualized as the motion of a representative point moving back and forth from one position on the potential energy curve to another. For example, for the same amount of excess vibrational energy, the vibrating atoms in a strong bond (Fig. 2.14, left) will experience a smaller displacement than the vibrating atoms in a weak bond (Fig. 2.14, right) because of the steeper “walls” of the potential energy curve on the left.

2.17 *The Quantum Mechanical Version of the Harmonic Oscillator*

With the classical harmonic oscillator of two vibrating masses as a model, we now consider the quantum mechanical system for a vibrating diatomic molecule. As for all quantum objects, the vibrating diatomic molecule is described by a vibrational wave function, χ . For a given electronic state, the wave function χ describes the shape (position in space relative to the electron cloud) and motion of the nuclei, just as Ψ describes the shape (position in space relative to the nuclei) of the electrons. We have discussed the orbital model for visualizing the electronic portion of a wave function. How can we visualize χ , the vibrational wave function and how do impose quantum mechanical effects on the classical harmonic oscillator?

Solution of the analogue of the electronic wave equation (Eq. 2.1) for a harmonic oscillator yields a set of vibrational wave functions χ_v each of which possesses a unique potential energy PE_v . Examination of the properties of the form of the vibrational wave functions leads to a picture of the vibrating diatomic molecule (a picture that is strikingly different from the classical harmonic oscillator for low-energy vibrations but becomes more analogous to the classical harmonic oscillator for high-energy vibrations). Let us now consider how to visualize the features of quantum mechanical features of a vibrating diatomic molecule, the quantization of the vibrational energy levels, and the wave-like character of the vibrations. This visualization of χ can be conveniently achieved by starting with a *classical* potential energy curve (Fig. 2.3), imposing quantization on the energy levels (Fig. 2.4), and then describing the appearance of the vibrational wave functions of the quantized energy levels (Fig. 2.5).

2.18 *The Quantized Vibrational Levels of a Harmonic Oscillator*

In quantum mechanics, as in classical mechanics, the starting model for a vibrating molecule is a harmonic oscillator which obeys Hooke's Law (Eq. 2.23). Solution of the wave equation (Eq. 2.1) for a harmonic oscillator obeying Hooke's law reveals that the energy levels are quantized and characterized by a quantum number, v (Fig. 2.4). The potential energy of a each vibrational level, PE_v , is given by Eq. 2.27, where v is the vibrational quantum number (which can take only integral values, 0, 1, 2, ...), ν is the vibrational frequency of the classical oscillator, and h is Planck's constant.

$$PE_v = h\nu(v + 1/2) \quad (2.27)$$

The important results derived from the quantum mechanical solution for the harmonic oscillator which contrast strikingly with the results for the classical harmonic oscillator are:

1. Only the quantized potential energy values, PE_v , given by Eq. 2.27 are possible (stable) for the allowed values of the quantum number v for the harmonically

- vibrating molecule, whereas the values of the potential energy for a classical harmonic oscillator are continuous and can take on any value depending on the energy available to the system.
2. The potential energy, PE_0 , of the lowest possible vibration is not zero (as it would be classically for a vibrating spring at rest), but is equal to $PE_0 = 1/2 h\nu$, *the zero point vibrational energy of a quantum harmonic oscillator*.
 3. For a harmonic oscillator the vibrational energy levels are equally spaced in units of $h\nu$ above the $v = 0$ level (whose energy is $1/2 h\nu$).
 4. Because of the inherent, irreducible zero point motion of all quantum particles, the nuclear motion of a vibration cannot be made to cease, i.e., the nuclei never stop fluctuating about the equilibrium position, so that their average kinetic energy, KE, can never equal zero. Zero point energy and zero point motion is an essential feature of every quantum particle, since a quantum particle never is at rest but will always vibrate (or oscillate) to a certain degree.

Figure 2.4 modifies the picture of the classical harmonic oscillator (Figure 2.3) by showing the form of the wave functions for each value of v on the corresponding energy level whose energy is E_v . In Fig. 2.4 the energies corresponding to representative values of v are indicated by horizontal lines (for $v = 0, 1, 2, 3, 4,$ and 10) for the two situations depicted in Figure 2.3 for the classical system. The amplitude (extent of the motion of a representative point that following the vibration from one extreme to the other) of the corresponding classical vibrational motion is obtained in Figure 2.3 from the intersection of the potential-energy curve with the corresponding energy level. The classical turning points of a vibration are the positions defining the maximum potential energy during a period of vibration. *At the turning points, the total energy of the oscillator is potential energy, because the two masses have stopped vibrating in one direction and are starting to vibrate back in the other direction. At the kinetic energy is therefore zero at the classical turning points.* Because the representative point is moving slowly near the turning points, the classical harmonic oscillator tends to spend most of its time at the turning points. It is important to note that the total vibrational energy, E_v (Eq. 2.27) is constant during the stretching and compression motions of the nuclei, but the kinetic

energy, KE, and potential energy, PE, are continually changing so that their sum equals (Eq. 2.26).

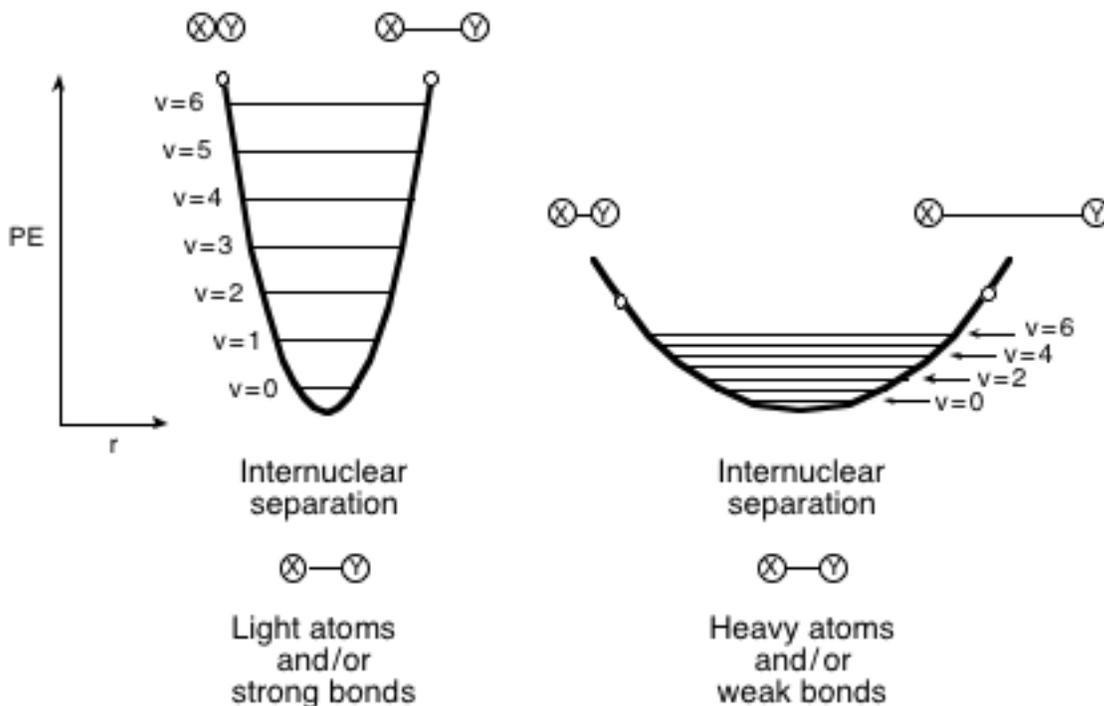


Figure 2.4 *Classical potential energy curve with quantized levels superimposed. See text for discussion.*

2.19 *The Vibrational Wave Functions for a Harmonic Oscillator. Visualization of the Wavefunctions for Diatomic Vibrations.*

The pictorial forms of the vibrational wave functions for a harmonic oscillator near the geometry of equilibrium separation are very non-classical and therefore, very non-intuitive. Thus, inspection of some pictures of vibrational wavefunctions will provide the student with some “quantum intuition” of how to visualize vibrational wavefunctions that will be very valuable in the interpretation of both radiative and radiationless transitions between vibrational levels of states (Chapter 3). The mathematical form of the vibrational wave functions χ_v for $v = 0, 1, 2, 3, 4$ and 10 are plotted qualitatively in Figure 2.5 (left) on the allowed (quantized) energy levels, which are indicated by horizontal lines. Recall that any wave, for example a sine wave, has an amplitude that

continuous oscillates from (mathematically) positive to (mathematically) negative values. The (mathematical) value of χ_v *above* the horizontal line is arbitrarily considered to be positive; the (mathematical) value of χ_v *below* the horizontal line is negative; and the (mathematical) value of χ_v *on* the line is zero, i.e., the horizontal line is a nodal line for the wavefunction for all levels above $v = 0$. The number of times that χ_v passes through zero equals v , the vibrational quantum number. It is important to note that the wavefunction for $v = 0$ does not possess a node. In this sense the wavefunction is analogous to the familiar wavefunction for a 1s electronic orbital, which does not possess a node. The mathematical sign of χ_v corresponds to the *phase* of the wave function at some point in space, r , during a vibration. The sign of χ_v is crucial when we consider that χ_v , a wave function, is not directly related to laboratory observation, but that a *product* of two wave functions is related to laboratory observation.

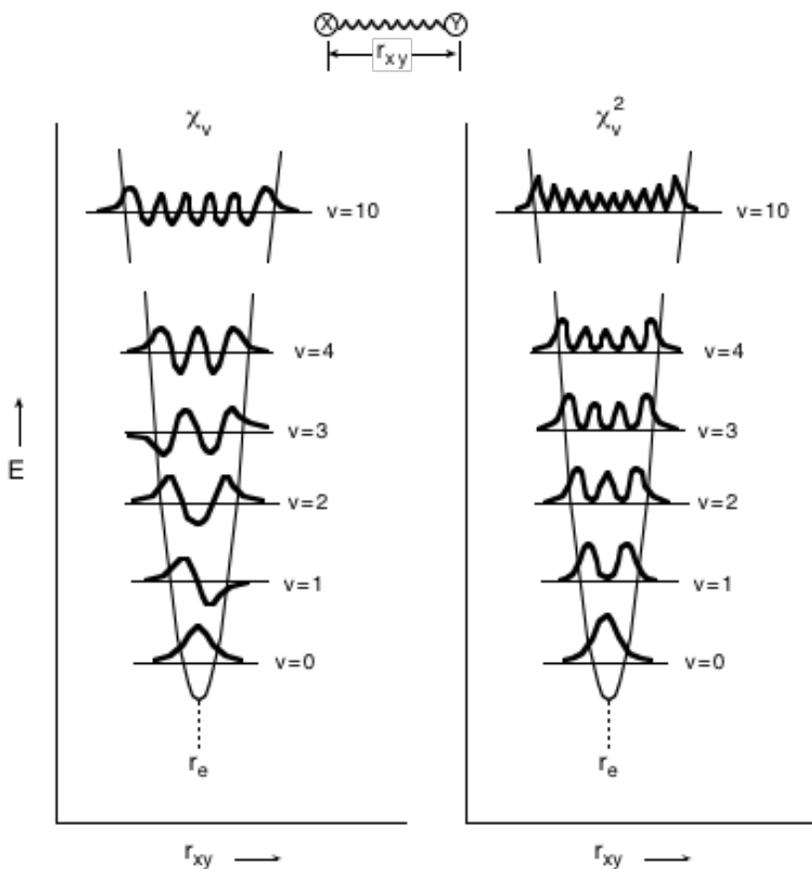


Figure 2.5. Quantum mechanical description of a vibrating diatomic molecule. See text for discussion.

Recall (Section 2.4) that the *square* of a wavefunction represents the probability of finding particles (electrons, nuclei) in space. Thus, function χ_v^2 (Fig. 2.5, right) represents the *probability* of finding the nuclei at a given value of r during vibration in a given level, i.e., a given value of v . We note that as one goes up the vibrational ladder, the wavefunction tends to have its highest density near the turning points of the classical vibration. In this limit the quantum vibration behaves similarly to the classical harmonic oscillator which spends most of its time at turning points. By examining Figure 2.5 (right) it can be seen that there is a finite, non-negligible probability that the atoms will vibrate **outside of the region defined by the classical potential-energy curve**. This peculiarity is the result of superimposing the wave description of the vibration and the classical picture. The wave description allows the nuclei to "leak out" of the boundary of the classical potential energy curve and explore a region of space greater than the classical description would allow.

Another peculiarity of the quantum mechanical model is apparent through inspection of the probability of finding the nuclei at a given separation for upper vibrational levels (Figure 2.5, right). In addition to the broad maxima of the probability distribution in the vicinity of the classical turning points that is expected from the classical model, a number of maxima (for $v > 1$) exist in between. For example, this means that for $v = 1$, there is a low probability of finding the vibrating atoms near r_e , whereas for $v = 2$, there is a relatively high probability of finding the vibrating atoms near r_e . Although the behavior of the harmonic oscillator is "peculiar" relative to the classical model for small values of v , as we go to higher and higher values of v , the quantum mechanical situation approximates the classical situation more closely (Bohr's correspondence principle), i.e., the atoms tend to spend more time near the turning points of vibration and very little time in the region about $r = r_e$, a situation similar to that expected for a classical vibration, i.e., A classical representative point has maximum kinetic energy near r_e and minimum kinetic energy at turning points.

The probability distribution curve for the $\nu = 0$ level in Figure 2.5 contrasts most dramatically with the classical picture. Instead of two turning points (as expected from the classical model), there exists one broad probability maximum at $r = r_e$. Classically, the vibrational state of lowest energy corresponds to the state of rest (point r_e in Fig. 2.16). This situation is impossible for the quantum mechanical model, since the position and velocity of this state would then be exactly defined (a violation of the uncertainty principle); as a result the vibrating quantum system always possesses a certain amount of zero point motion. *We shall learn in Chapters 4 and 5 that radiative and radiationless transitions in condensed phases originate from thermally equilibrated vibrational states, which means that the structure of the $\nu = 0$ level will be of great importance in organic spectroscopy and photochemistry.*

Based on the above descriptions we have built up an important “quantum intuition” based on the quantization of vibrational energy levels and on visualizing the wavefunctions of the quantum harmonic oscillator shown in Fig. 2.5. We can now transfer comfortably and smoothly from the classical description of a “dynamic” representative point moving on the surface to the quantum description of a “static” probability of finding the nuclei in a certain region of space with a given motion and phase. In Chapter 3 we shall employ these ideas to generate a model for an understanding of the factors determining the probability of transitions between vibrational levels of different electronic states.

2.20 A First Order Improvement of the Harmonic Oscillator Model. The Anharmonic Oscillator

The harmonic oscillator is a Zero Order approximation for a vibrating diatomic molecule X-Y (and for the vibrations of an organic molecule). However, the simple model fails for nuclear geometries corresponding to severe compressions and especially for severe elongations of the X-Y bond. In these cases the restoring force does not obey Eq. 2.23. For example, when a bond has been extended to, say, 2 or 3 times its normal length (from 1-2 Å to 5-6 Å), the atoms X and Y experience very little “restoring” force, i.e., the bond is essentially broken and the atoms may fly apart and the restoring force is

zero for longer separations after the bond has broken. For an ideal harmonic oscillator, the restoring force increases indefinitely and smoothly with increasing or decreasing distance from the equilibrium position (see Figs. 2.3, 2.4 and 2.5). For a real molecule, however, the potential energy will rise more gradually than predicted by $PE = 1/2kr^2$ (Eq. 2.24) because of a weakening of the X-Y bond at large r , as is shown in Figure 2.6 for the HCl diatomic molecule. The “anharmonic oscillator” takes these factors into account in the First Order corrections to the Zero Order harmonic oscillator model. For the anharmonic oscillator as the X-Y bond stretches, the potential energy reaches a limiting value (the PE of the bond or the bond energy), the restoring force disappears, and the HCl bond breaks. Thus, the energy of the asymptote in Figure 2.6 corresponds to the dissociation energy of the molecule. If the energy of the system just corresponds to the asymptote, the atoms at a great distance from one another will have zero velocity. A point above the asymptote corresponds to a situation for which the kinetic energy (which is essentially continuous) of the two atoms is increased. On the other hand, compression of the nuclei results in a more rapid increase in potential energy than is predicted by the harmonic oscillator, because of the sudden rise of electrostatic repulsions with decreasing nuclear separation.

Recall (Eq. 2.26) that the sum total vibrational energy of the system equals the sum of the kinetic and potential energy. For example, in the $v = 3$ vibration level, the anharmonic oscillator shown in Figure 2.6 possesses $40 \text{ kcal/mole}^{-1}$ at a point A (all potential energy), while at point B the system possesses about $35 \text{ kcal/mole}^{-1}$ of kinetic energy and 5 kcal/mole^{-1} of potential energy (relative to an arbitrary energy of zero for the lowest point in the curve).

Another important feature of the anharmonic oscillator is that its vibrational levels, although quantized, are not equally separated in energy, which contrasts with the situation for the harmonic oscillator (Fig. 2.4). The energy separations decrease slowly with increasing v , as shown in Figure 2.6. For example, for HCl the energy separation between $v = 0$ and $v = 1$ is about $12 \text{ kcal/mole}^{-1}$, while the energy separation between $v = 10$ and $v = 11$ is only about 5 kcal/mole^{-1} .

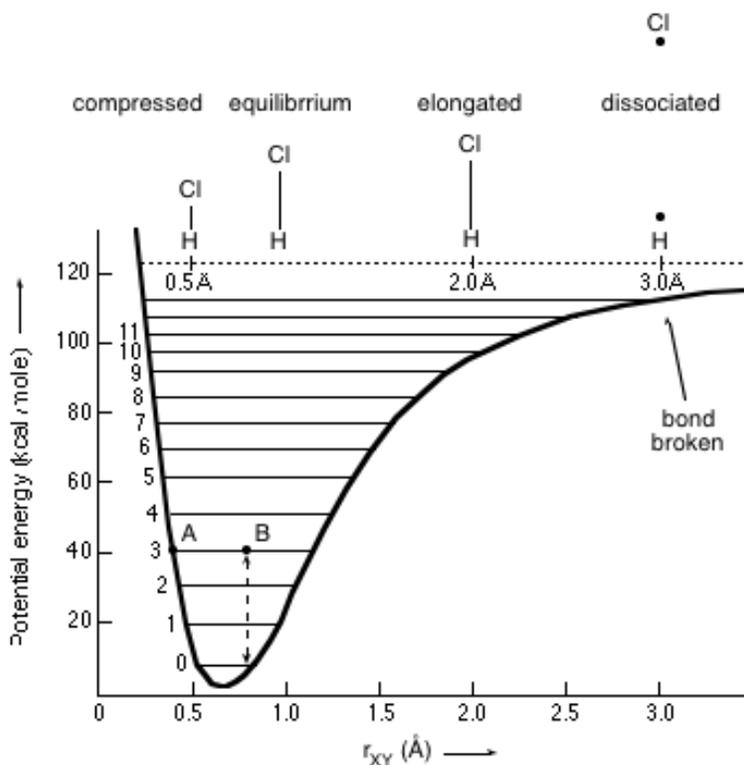


Figure 2.6. *Quantized potential energy curve for HCl.*

2.21 Summary. Building Quantum Intuition for Vibrational Wavefunctions

Although understanding and use of the paradigm of quantum mechanics requires a sophisticated mathematical background, the wave functions of electrons, spins and vibrations may be approximated by pictorial representations that are useful for understanding the qualitative aspects of organic photochemistry. In this chapter we have obtained some quantum intuition concerning the behavior of the wavefunctions of vibrating molecules through quantizing the energy levels of the harmonic oscillator and visualizing the vibrational wavefunctions. In Chapter 3 we shall use this quantum intuition to examine how vibrational wavefunctions influence the rates of transitions between vibrational states of different electronic states.

2.22 *Electron Spin. A Vector Model for Visualizing Spin Wavefunctions*

In this Chapter we have seen how the orbital description of electrons allows a visualization the electronic wave function (ψ) of the location of electrons in space and that provides quantum intuition for examining electronic issues such as orbital overlap and features of interactions of electrons that are important in determining the ranking of electronic energies corresponding to different electronic configuration and estimation of the electron exchange energy. We have also developed a model of vibrational wave functions (χ) that allows a visualization of energy levels of vibrating nuclei with the harmonic oscillator or a Zero Order approximation. This model provides quantum intuition concerning vibrations of molecules near the zero point ($v = 0$) level and will be a powerful means of appreciation of both radiative transitions (Chapter 4) and radiationless transitions (Chapter 5) between electronic states.

In addition to visualizing the orbital nature of electrons and vibrating nuclei, we also need to visualize the nature of the electron's spin wavefunction, \mathbf{S} (Eqs. 2.7 and 2.8), and to develop a working description of the spin structure of molecules that is needed for an understanding of the mechanisms of transitions between singlet states (S_n) and triplet states (T_n). Since electron spin is a topic only briefly covered in elementary texts, we shall develop a relatively detailed model of the electron spin wave functions, \mathbf{S} , that is as pictorial as the orbital model, Ψ , and the harmonic oscillator model for the vibrational wave function, χ . This model of electron spin, which is based on the properties of vectors, will provide use with quantum intuition concerning the properties of the spin vibrational wavefunction, \mathbf{S} . It is of interest to note that the language of the vector model for electron spin is readily transferable for the description of nuclear spins, the key objects of interest for NMR spectroscopy.

Electron spin is considered in quantum mechanics to be a manifestation of a fundamental property of electrons (just as the mass and charge of an electron is a fundamental property), namely the inherent *spin angular momentum* of an electron. Our visualization of electron spin will employ the concept of classical angular momentum, which is the property of a macroscopic object which is in a state of rotation about an axis. As we have done previously, in order to develop a quantum mechanical picture of electron spin angular momentum (when the word spin is used we mean spin angular momentum and its implied magnetic and energetic characteristics to be discussed below),

we first appeal to a classical model of angular momentum and then modify this model with the appropriate quantum characteristics.

Two important classes of classical angular momentum involve (1) the circular “orbital” motion of a particle rotating at a fixed distance about a center and (2) the circular “spin” motion of a rotating sphere (or a rotating cylinder) about a defined axis (arbitrarily termed the z-axis). We shall return to case 1 later in this Chapter (when we deal with electron orbital angular momentum), but we shall first deal with case 2, which is relevant to electron spin. Taking a concrete physical model of an electron as a sphere of negative electricity, the **spin** of an electron is the angular momentum resulting from its spin motion about an arbitrary axis. Although a classical spinning electron could be imagined to possess different values of angular momentum depending on the velocity and direction of its spinning motion, quantum mechanics considers electron spin as an **intrinsic angular momentum** which is a fixed and fundamental characteristic of an electron, similar to its fixed and fundamental charge or mass. Specifically, an electron possesses a fixed and characteristic amount of spin angular momentum (or spin, for brevity) of exactly $(1/2)\hbar$ (\hbar , Planck's constant, h , divided by 2π , is the fundamental quantum mechanical unit of angular momentum) whether it is a "free" electron not associated with any nucleus, or whether the electron is associated with a nucleus in an atom, a molecule, an electronically excited state, or a radical. The spin angular momentum of an electron is *always* the same, **exactly** $1/2 \hbar$, whatever orbital the electron happens to occupy. Thus, an electron in the n-orbital of a n,π^* state has the same spin as the electron in a π^* orbital of a n,π^* state. Both have a spin of $1/2$ (when dealing with spin, **S**, the units of \hbar will be assumed).

When two or more electron spins interact, according to the laws of quantum mechanics, only certain values of the **magnitude** of the net spin angular momentum (**S**) are allowed. These values are given by $S = [S(S + 1)]^{1/2}$ (units of angular momentum understood), where S is the spin quantum number and may be 0, a positive integer or $1/2$ a positive integer. In photochemistry the most important values of the spin quantum number S are 0, $1/2$ and 1, corresponding to singlet states, S (0 spin angular momentum),

doublet states, D (1/2 unit of spin angular momentum) and triplet states, T (one unit of spin angular momentum).

We have seen (Section 2.7) that electronically excited states, *R , possessing the same orbital configuration, may exist with different spin configurations of the orbitally unpaired electrons, i.e., a singlet spin configuration, S_1 , in which the electron spins are "antiparallel" ($\uparrow\downarrow$) for which there is no net spin and a triplet spin configuration, T_1 , in which the electron spins are "parallel" ($\uparrow\uparrow$) and for which there is a net spin of $1\hbar$. We now show how to visualize the "antiparallel" and "parallel" configurations of two electron spins **by appealing to the classical vectorial properties of an object executing a spinning motion about an axis, such as a top or a gyroscope**. We shall review the fundamental classical properties of vectors that are important for an understanding of electron spin and then describe the quantum mechanics of spin in terms of this vector description.

Since we are interested in the relative energies associated with different spin configurations and states, we will find it convenient to describe the interactions between electron spin as those between **spin magnetic moments** (μ) that we shall directly relate to the **spin angular momentum** (S). The idea behind this tactic is that we can build an intuition for the energy of interactions of two magnets and relate that energy to the interactions of two spins interacting. It should be born in mind however, that angular momentum is the fundamental property of electron spin and magnetism is a convenient framework to discuss the measurable properties of spin qualitatively and quantitatively. For simplicity, we shall use the same symbol, S , to describe the spin wavefunction and the quantity, the spin angular momentum.

2.23 A Vector Model of Electron Spin

Some physical quantities are termed *scalars* if they can be completely described by a magnitude, i.e., a single number and a unit. Examples of scalar quantities are energy, mass, volume, time, wavelength, temperature, and length. However, in order to describe certain physical quantities in addition to a magnitude we must also specify a **directional quality**. Quantities which require both a magnitude and a direction for

complete characterization are termed mathematically as **vectors**. Examples of vector quantities are velocity, electric dipoles, angular momentum, magnetic fields, and magnetic dipoles (also termed magnetic moments). When dealing with spin we shall represent *scalar* quantities in *italics* and **vectors** in **bold face type**. For example, spin angular momentum is a vector quantity and is given the bold face symbol **S**, whereas the magnitude of the spin angular momentum is a scalar quantity and is given the italics type symbol, *S*.

Both angular momentum and magnetic moments are vectors and may be completely characterized by a *length* and a *direction*. It is natural, therefore, to seek a vectorial representation of electron spin and to apply vectors to visualize spin angular momentum **S** and the magnetic moments μ resulting from spin angular momentum. The interactions between magnetic vectors will determine the *magnetic* energies of spin state possessing two or more interacting electron spins.

When a physical property can be characterized by a vector, the powerful and simple shorthand rules and algebra of vector mathematics can be employed to describe and analyze the physical quantities in a completely general manner independent of the specific quantity the vectors represent. Thus, the same rules of vectors apply to electron spins and nuclear spins, to angular momentum, to electric dipoles and to magnetic fields. In contrast to the physical space about the nuclear framework occupied by electrons, it is useful to think of vectors as existing in a "vectorial space", i.e., independent of the three dimensional space occupied by the physical object, although it is convenient to place the vectors in a coordinate system which corresponds to a coordinate system that pertains to the molecule x, y, z axis. Vector notation will assist in visualizing the wavefunctions for electron spin and providing quantum intuition for spin in the same way that 3-D representations of molecular orbitals assist in the visualization of electronic wave functions.

2.24 Definition and Important Properties of a Vector.

We shall review briefly some properties of vectors that will be used repetitively in description of the properties of electron spin and interacting electron spins. Vectors are

conveniently represented by an "arrow". The arrowhead of a vector indicates the sense of the direction relative to a reference axis (conventionally termed the Cartesian z-axis) and the length of the arrow represents the magnitude of a physical quantity represented by the vector. The orientation of the vector in space is defined in terms of the angle, θ , that the vector makes with the z-axis. Interacting vectors must all relate to the same axis system. If the vectors do not interact, each may have its own arbitrary axis system.

2.25 *Vector Representation of Electron Spin*

Let us consider some important properties of all vectors, with a vector representation of spin angular momentum \mathbf{S} as a concrete exemplar. Figure 2.7 summarizes the well trigonometric relationships of a spin vector, \mathbf{S} , that makes an angle θ with the z-axis. The important vectorial properties are : (1) \mathbf{S} possesses a component, \mathbf{S}_z on the z-axis: (2) \mathbf{S} possesses a component $\mathbf{S}_{X,Y}$ in the x,y plane; and (3) the magnitude of the component on the z-axis is related to the magnitude of the spin by the trigonometric Eq. 2. 28, where $|\mathbf{S}_z|$ is the magnitude (absolute value) of the vector on the z-axis and $|\mathbf{S}|$ is the magnitude of the spin vector.

$$\cos\theta = |\mathbf{S}_z|/|\mathbf{S}| \quad (2.28)$$

The uncertainty principle allows only one component (\mathbf{S}_z or $\mathbf{S}_{X,Y}$) of the spin vector to be specified exactly (conventionally the z-component is the component selected) the position (termed the azimuth of the vector) of the vector in the xy-plane is completely undetermined. This is why only the z axis is employed and specified when discussing the energies of interacting spin states.

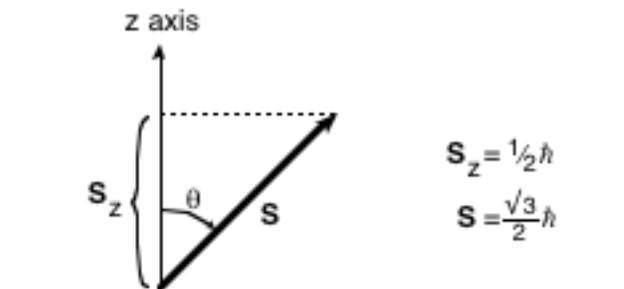


Figure 2.7. Trigonometric relationships between the spin vector, S , and the z axis.

We shall now consider the vector representation of **quantized** electron spin in some detail for the two most important cases in photochemistry: a single spin and two interacting spins which be coupled as parallel ($\uparrow\uparrow$) or antiparallel spins ($\uparrow\downarrow$). We shall the latter description is essentially two dimensional and that for the 3D representation of interacting spins, these two cases requires a modification of the terms “parallel” and “antiparallel” when referring to spin configurations of singlets and triplets.

2.26 Vector Model of a Quantized Single Electron Spin. Spin Multiplicities

As mentioned above, the **uncertainty principle** of quantum mechanics requires (1) that an exact measurement of the electron spin can be made only of one component (on the z -axis), leaving the values of the electron spin in the x,y plane completely unknown and (2) that the values of \mathbf{S} and (therefore of \mathbf{S}_Z) are quantized. The value of \mathbf{S}_Z is exactly $1/2 \hbar$ (values of \mathbf{S} will always be in units of \hbar). Since the vector \mathbf{S} representing the spin cannot lie exactly on the z -axis (for then its exact value on all three axis would be known precisely, in violation of the uncertainly principle), the magnitude of \mathbf{S} must be somewhat greater than $1/2 \hbar$ and the vector representing the spin must make a precise angle θ with the z -axis so that the value of \mathbf{S}_Z becomes exactly $1/2 \hbar$ on the z -axis. The electron is imagined to be a spinning spherical electrically charged mass that generates angular momentum as a result of its rotational motion. In Figure 2.8 we show the angular momentum vector pointing perpendicular to the plane of rotation of a spinning spherical electron, a feature based on analogy to classical angular momentum of a spinning sphere.

Recall that quantum mechanics requires that the value of the spin angular momentum vector be limited to magnitudes determined by the relationship $\mathbf{S} = [S(S+1)]^{1/2}$, where S is the spin quantum number. The spin quantum number, S , of a single electron is $1/2$ (S is a pure number). Thus, according to spin quantum mechanics, the actual value of the length \mathbf{S} for a single electron is given by $(1/2(1/2 + 1))^{1/2} = (3/4)^{1/2}$. There is only one angle, θ , for which the value of \mathbf{S}_Z on the z -axis will be exactly $1/2$ if

the length of the vector is $(3/4)^{1/2}$. From Eq. 2.28, the angle θ that the vector \mathbf{S} must make with the z-axis in order that S_z is exactly $1/2$ is about 71° (i.e., from Eq. 2.28, $S_z \cos\theta = S$, $(1/2) \cos 71^\circ = (3/4)^{1/2}$). Because of the trigonometric relationships of vectors, the vectorial representation of spin results in the peculiar "square root" relationship between the spin and its component on the z-axis. The length of a single electron spin \mathbf{S} is a fixed quantity **independent of its orientation**, since quantum mechanics requires the vector to maintain a fixed angle to the z-axis. *It should be noted that any particle with spin 1/2 possesses the same value of angular momentum, namely $1/2 \hbar$.* Thus, electrons, ^1H nuclei and ^{13}C nuclei all possess the same value of spin angular momentum, exactly $1/2 \hbar$.

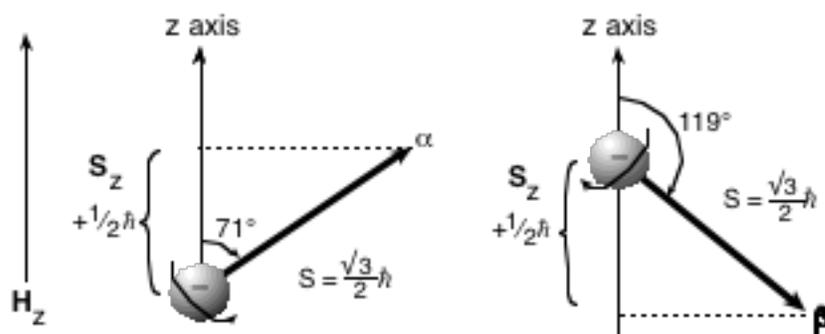


Figure 2.8. *Vector representation of a spin 1/2 particle (an electron, a proton, a ^{13}C nucleus). The symbol α refers to the spin wave function of a spin with $M_s = +1/2$ and the symbol β refers to the spin wave function of a spin with $M_s = -1/2$. See text for discussion.*

The number of quantum mechanically allowed orientations of a given state of spin angular momentum consisting of more than one electron is termed the **multiplicity** of the state. The multiplicity of a spin state is computed from the spin angular momentum quantum number, S according to Eq. 2.26.

$$\text{Spin Multiplicity} = 2S + 1 \quad (2.29)$$

There are three spin situations of greatest importance to organic photochemistry: (1) $S = 0$; (2) $S = 1/2$; and (3) $S = 1$. From Eq. 2.29 the multiplicity for $S = 0$ is 1 (termed a singlet state, S); the multiplicity for $S = 1/2$ is 2 (termed a doublet state, D); and for $S = 1$ the multiplicity is 3 (termed a triplet state, T). We have employed the terms

singlet and triplet earlier in the text and shall now show their relationship to the number of possible spin states through the vector model.

It is conventional and convenient to term the spin wave function corresponding to the quantum number $M_S = +1/2$ is given the symbol α , and the spin wave function corresponding to $M_S = -1/2$ is conventionally symbolized as β . We shall use the terms α spin and β spin in reference to these wave functions and consider the vector representation in visualizing the wave functions.

2.27 Vector Model of Two Coupled Electron Spins. Singlet and Triplet States

We now consider the important interaction or coupling of two single spins, a situation that is important in describing an electronically excited state *R (or reactive intermediate I), which possesses two orbitally uncoupled electrons. The spin configurations of two electrons in singly occupied orbitals are not restricted by the Pauli Principle, i.e., a singlet or a triplet configuration are both allowed. The quantum mechanical rule for the possible couplings of two $1/2$ spins of the two orbitally uncoupled electrons is very simple: The final **total** angular momentum (units of \hbar) of a two spin system is either 0 (singlet, S) or 1 (triplet, T).

We now shall use the vector model of spin to visualize the singlet and triplet states that result from the coupling of two electron spins which occupy separate orbitals. The singlet state results from the coupling of an α spin and a β spin in such a way that the spin vectors are antiparallel (commonly depicted as $\uparrow\downarrow$) and collinear and the angle between the heads of the vectors is 180° (Figure 2.9a). Such an orientation of vectors clearly results in exact cancellation of the net spin angular momentum of the spin vectors, so the net spin vector length is 0. This means that the net spin of the singlet state, as expected, is exactly equal to 0. Although a specific arbitrary orientation of the two spin $1/2$ vectors is shown in Figure 2.9a, there is no preferred orientation at all since all orientations yield zero spin angular momentum. So, we conclude that the singlet state has no net spin and no preferred orientation of the component spin vectors, even though it is composed of two electrons each of which possesses a spin of $1/2$. This situation is analogous to the cancellation of dipole moments in a linear molecule such as $O=C=O$

which has two polar bonds, but no net dipole moment. All electrons that are paired in an orbital are required by the Pauli Principle to be in a singlet state and therefore will have their spin vectors oriented as shown in Figure 2.9a. As a result, since nearly all organic molecules possess two electrons in each orbital in their ground states, organic molecules typically possess singlet ground states.

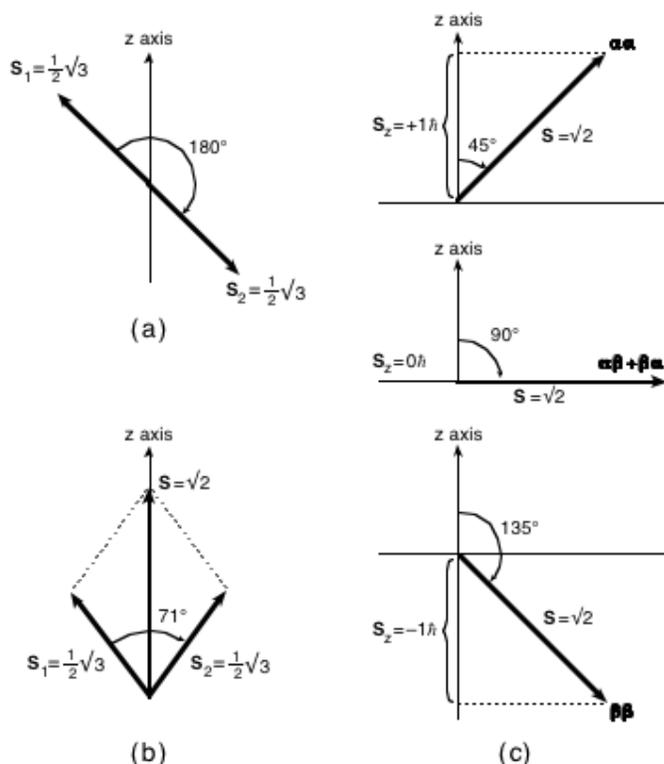


Figure 2.9. *Subtraction and addition of two spin 1/2 particles. Upon subtraction, the spins exactly cancel (a). Upon addition, the spin vectors add up (b) to a total length of $(2)^{1/2}$, but have a projection (right) of 1, 0 and -1 on the z-axis (c).*

The triplet state (for which $S = 1$) *also* results from the coupling of an α spin and a β spin, but this time the coupling is such that the spin vectors make an angle between the vectors which is 71° (Figure 2.9b). In Section 2.27 we shall see that the angle of 71° is required by trigonometry so that the two spin 1/2 vectors will couple vectorially to produce a single spin equal to a vector with a value of $S = 1$ on the z-axis. According to quantum mechanics the values of the spin on the z-axis for a $S = 1$ system can be $S_z = +1 \hbar$, $S_z = 0 \hbar$ or $S_z = -1 \hbar$. These spin states are assigned the quantum numbers $M_S = +1$,

$M_S = 0$ and $M_S = -1$ (the symbol M is derived from the *m*agnetic properties of the magnetic dipole associated with oriented spins), respectively, and are termed the sublevels of the triplet state. The origin of the term “triplet state” is based on the quantum mechanical requirement that a $S = 1$ spin state must possess three energy sublevels corresponding to the three quantum numbers, $M_S = +1$, $M_S = 0$ and $M_S = -1$. From trigonometry (Eq. 2.28) the angle θ that the vector must make with the z-axis to achieve the values of $+1 \hbar$, $0 \hbar$ or $-1 \hbar$ are 45° , 90° and 135° , respectively (Figure 2.9c).

Now we can see clearly how the vector model and trigonometry provide a vivid means of visualization of singlet and triplet spin states based on the rules of quantum mechanics. For $S = 0$, the coupled spins exactly cancel and there is no net spin anywhere in space and only **one** spin state, a *singlet* state (quantum number $M_S = 0$) results. For $S = 1$, the coupled spins add to one another and there are **three** spin states allowed by quantum mechanics corresponding to the three quantum numbers $M_S = +1$, $M_S = 0$ and $M_S = -1$.

You will recall that the spin wave function α describes an “up” spin and that the spin wave function β describes a “down” spin. Notice that **both** the singlet state and the triplet component with $M_S = 0$ possess one α spin and one β spin. Thus, a simple two dimensional up-down "arrow" notation ($\uparrow \downarrow$) would make the singlet state ($M_S = 0$) and the $M_S = 0$ level of the triplet appear to be identical in terms of spin characteristics, even though the singlet has no net spin and the $M_S = 0$ level of the triplet possesses a net spin of $1\hbar$! It is important to realize that this distinction between the $M_S = 0$ for the singlet and triplet is made only in the three dimensional vector representation which we shall describe in the next section. This situation of the failure of the two dimensional representation of spin to distinguish the $M_S = 0$ if the triplet state from the singlet state is somewhat analogous to the failure of two dimensional representations of molecular structure to distinguish two enantiomeric centers in molecules.

Now we have to deal with an interesting mathematical modification of our α and β label of spins for the singlet state and the $M_S = 0$ level of the triplet state that is imposed by the Pauli Principle and electron exchange (Section 2.9). Because of the latter, we cannot label the wavefunctions of the two states with one spin up and one spin

down as either $\alpha_1\beta_2$ or $\beta_1\alpha_2$, as this would imply that we can distinguish electron 1 and electron 2 as being in a specific and differentiable spin state. This violates the Pauli Principle which states that electrons are indistinguishable upon exchange of coordinates. Quantum mechanics allows that an acceptable spin wave function for the singlet state is $(\alpha_1\beta_2 - \beta_1\alpha_2)$ where the minus sign signifies that the two spins are exactly 180° *out of phase* (a mathematical "normalization" factor of $(1/2)^{1/2}$ is of no interest for our qualitative discussion and is therefore ignored) An acceptable spin wave function for the triplet state is $(\alpha_1\beta_2 + \beta_1\alpha_2)$, where the plus sign signifies that the two spin are *in phase* and couple to generate a net spin of 1. Thus, we will let the singlet state, S, be represented by the symbols $\alpha\beta - \beta\alpha$ and the triplet state, T, will be represented by the symbols $\alpha\beta + \beta\alpha$. Both of these states have the same quantum number $M_S = 0$, but possess different wavefunctions.

We can think of the minus sign in the singlet function $\alpha\beta - \beta\alpha$ as representing the "out of phase" character of the two spin vectors causing the spin angular momentum of the individual spin vectors to exactly cancel (Fig. 2.9a) and the plus sign in the triplet wave function as representing the "in phase" character causing the individual spin vectors to add together and reinforce each other (Fig. 2.9 b).

There is no ambiguity for the $T_+(\alpha\alpha)$ the triplet with two spins up ($\alpha\alpha$ or $M_S = +1$) or for $T_-(\beta\beta)$ the triplet state with two spins down ($M_S = -1$). For the state with $M_S = +1$, the spin function $\alpha\alpha$ is acceptable because, since both electrons possess the same orientation, we need not need to attempt to distinguish them upon exchange. The same holds for the $M_S = -1$, for which the spin function $\beta\beta$ is acceptable to the Pauli Principle.

2.28 The Uncertainty Principle and Cones of Possible Orientations for Electron Spin 1/2

So far we have discussed the spin vectors in terms of a two dimensional representation, and now proceed to a more realistic model of the spin vector in 3-D relative to the z-axis. As we have seen, according to the Uncertainty Principle of quantum mechanics, if the value of S_z on the z-axis is measured precisely, the 3D

position of \mathbf{S} , i.e., its directional angle of \mathbf{S} in the x,y plane (termed the azimuthal angle) cannot be determined at all. Thus, when S_z is measured there is no information at all that can be obtained experimentally concerning the azimuthal angle of \mathbf{S} . In terms of the vector model, this means that an up spin, which makes a specific angle of ca 71° with the z-axis and a value of $S_z = 1/2$, may project to any azimuthal angle in the x,y plane. Thus, there is a set of positions in space making an angle of ca 71° with the z-axis, any one of which could correspond to the actual position of the spin vector. *This set of possible positions constitutes a cone such that whatever the specific position the spin vector takes on the cone, the angle of the vector with the z- axis and the projection of the vector on the z-axis are always the same, 71° and $1/2$; however, the x and y components or the vector are completely undetermined.* Such a cone is termed the **cone of possible orientations of an α spin ($M_S = +1/2$)**. Figure 2.10 (left top) shows the cone of possible orientations of an α spin with one possible arbitrary orientation being shown explicitly. Although we can be sure that an α spin will lie in this cone, we cannot specify where. A corresponding cone of possible orientations (Figure 2.10, left middle) exists for a β spin with one possible arbitrary orientation being shown explicitly.

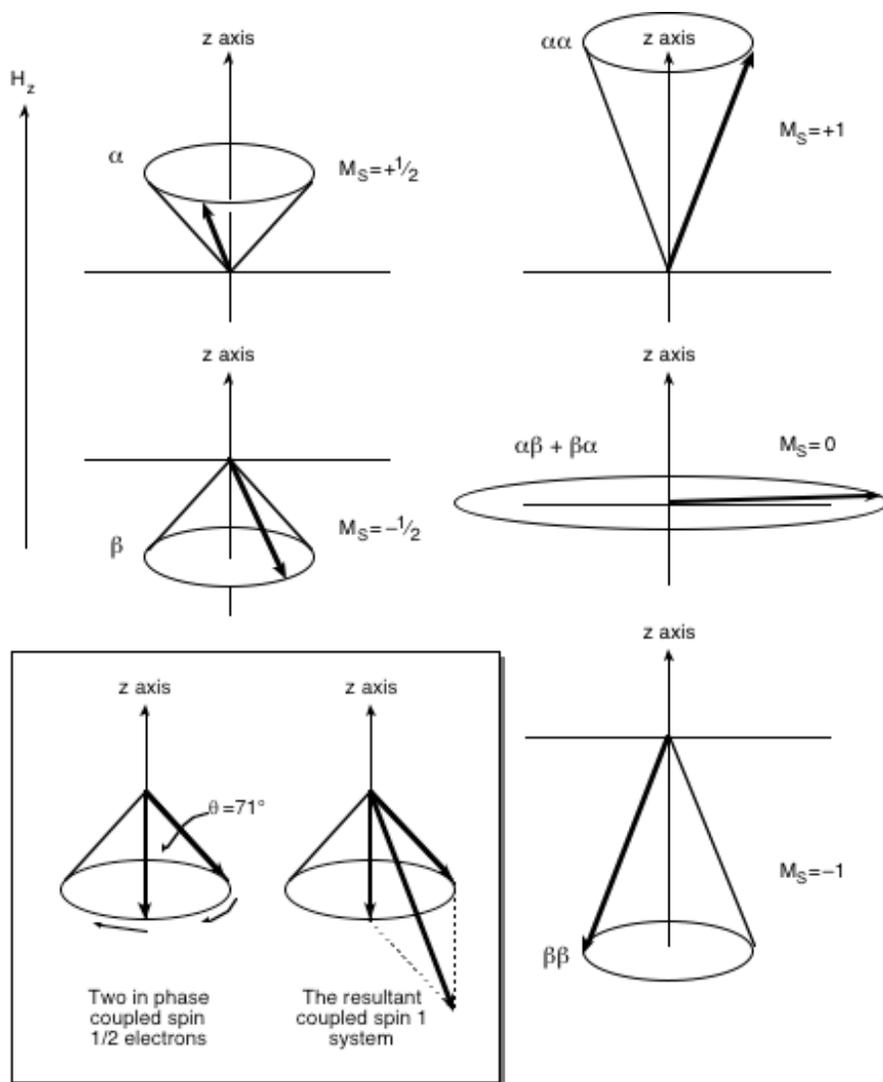


Figure 2.10 Cones of possible orientation for a spin 1/2 (left) and spin 1 (right) system of angular momentum. An arbitrary position of the spin vectors is shown for each of the possible cones. See text for discussion of the insert.

In the absence of an interacting magnetic field, the vector representing the angular momentum is imagined as being stationary and "resting" somewhere in the cone of possible orientations. If a coupling magnetic field is applied (e.g., a static applied laboratory field, or an oscillating applied laboratory field, or fields due to the magnetic moments generated by the motion of spins in the environment, etc.) the coupling will cause the spin vector to sweep around the cone, a motion of the spin that we shall refer to as precession. We shall consider spin precession in Chapter 3 when we consider

transitions between magnetic states. For now we will only describe the “static” magnetic states and the energies associated with them.

2.29 *Cones of Possible Orientations for Two Coupled 1/2 Spins*

In photochemistry *R is generally a singlet state or a triplet state possessing an electronic configuration that is approximated by two singly occupied orbitals such as a n,π^* or a π,π^* configuration. In these cases the two electron $1/2$ spins can be viewed as being coupled to produce a net spin of 1 (triplet) or a net spin of 0 (singlet).

Let us now consider the possible orientations in the case of the triplet of $S = 1$ (Figure 2.10, right). The situation with respect to a cone of possible orientations of the spin 1 is analogous to that for the spin $= 1/2$ case in the cases of $M_S = +1$ ($\alpha\alpha$) and $M_S = -1$ ($\beta\beta$), for which "up" and "down" cones of possible orientations are shown in Fig. 2.10. In the case of $M_S = 0$ ($\alpha\beta + \beta\alpha$), the spin vector lies not in a cone, but in a **circle** of possible orientations lying in the x,y plane (Figure 2.10, right middle). An interesting feature of this case is that the projection of the spin on the z-axis is $0 \hbar$, even though the length of \mathbf{S} is $1.7 \hbar$. It should be noted that the magnitude of the spin vectors for $S = 1$ are larger ($1.7 \hbar$) than those for $S = 1/2$ ($0.87 \hbar$), although by convention the units are not usually explicitly shown in the figures. We also note that for the singlet state, strictly speaking since the value of the spin vector is zero, there is no cone of orientation because the vector length is zero. However, it is convenient when discussing two weakly coupled spin $1/2$ systems to consider a cone of possible orientations that is determined by the two $1/2$ spins (Fig. 2.10)

Finally, we can employ the cone of possible orientations to represent two coupled $1/2$ spins to make the point mentioned above concerning the requirement that two $1/2$ spins must be precisely **in phase** in order to produce a spin 1 state. In this case there are two requirements to make the eventual value of the spin on the z-axis exactly equal to 1: (1) the angle between the two spin $1/2$ vectors must add vectorially to yield a resultant vector of length equal to $1.7 \hbar$ and (2) the angle that this resultant vector makes with the z-axis must be 45° , 90° or 135° in order for the projection of the vector on the z-axis to

be exactly $+1 \hbar$, $0 \hbar$, or $-1 \hbar$, respectively. It is important to note that the downward rotation of the vector from the $M_S = 1$ state by 45° produces the $M_S = 0$ state and a change of exactly 1 unit of spin angular momentum ($\Delta S = 1$). Similarly, downward rotation of the $M_S = 0$ state by 45° produces the $M_S = -1$ state and a change of exactly one unit of angular momentum. ***Changes in angular momentum of spin states must occur with conservation of angular momentum and typically occur with a change of one unit of spin angular momentum*** (which is exactly compensated by a change in angular momentum of exactly one unit in the coupled system).

Up to this point in the text we have used the term “parallel” spins ($\uparrow\uparrow$) to describe two coupled $1/2$ spins in a triplet state. To have the appropriate resultant, two coupled spin $1/2$ systems must make an angle of ca 71° with one another (Fig. 2.10). We now see that the term “parallel” spin actually refers to the condition that the spins make an angle of 71° with one another. Importantly, it should be noted that the spins for the $\alpha\alpha$, $\beta\beta$ and $\alpha\beta + \beta\alpha$ are all at an angle of 71° . Thus, only loosely speaking are the two spins are parallel for each case.

2.30 Summary

The angular momentum of a rotating or spinning electron or group of coupled electron spins is conveniently and mathematically represented by a vector \mathbf{S} which according to quantum mechanics must have a length of exactly, $[S(S + 1)]^{1/2}$ where S is the electron spin quantum number of the system. Following the rules of quantum mechanics, the vector representing the angular momentum due to electron spin can only possess certain quantized values and any particular observable value corresponds to specific orientations of the spin vector in space. Since only one component of a spin vector (conventionally the z-axis) can be observed experimentally according to the uncertainty principle, the azimuth of the vector (its orientation in the xy plane, called its azimuth) is completely unknown. However, the spin vector must be oriented in one of the cones of orientation at the specific angles allowed by quantum mechanics.

The vector model for spin angular momentum allows a clear visualization of the coupling of spins to produce different states of angular momenta. Chemists are

accustomed to discussing states in terms of their energies and not their angular momentum. We now need to connect the vector model of angular momentum with models that allow us to deduce the magnetic energies and how these energies are related to the orientations of the spin vector in space. Then we shall be in a position not only to rank the magnetic states in terms of their energies (a goal of this Chapter) but also to understand the dynamics of transitions between magnetic states, (a goal of Chapter 3).

2.31 *The Connection between Angular Momentum and Magnetic Moments. A Physical Model for an Electron with Angular Momentum.*

We shall now develop a physical model for electron spin concentrates on the *magnetic properties* and the *magnetic energies* associated with spin angular momentum. Electrons and certain nuclei (^1H , ^{13}C), possessing both electrostatic charge and spin angular momentum, also possess magnetic moments (i.e., magnetic dipoles, which are vectors analogous to electric dipoles) that interact with each other and with applied laboratory magnetic fields. We will now examine the connection between spin angular momentum and the magnetic moments associated with spin. We shall consider first apply the vector model to a familiar physical model of a magnetic moment resulting from orbital motion of an electron in a Bohr orbit. ***This concrete physical model allows us to compute the magnetic moment of the orbiting electron in terms of its orbital angular momentum.*** With this connection between orbital angular momentum and magnetic moments, we shall see how this result can be used to generate a connection between spin angular momentum and magnetic moments.

We have seen how to qualitatively rank the relative energy of electronic orbitals and electronic states based on the Aufbau principle and Pauli Principle (Section 2.7). We also learned how to qualitatively rank the relative energies of vibrational levels based on their quantum number and number of nodes in their wavefunctions (Section 2.2.17). It would clearly be useful to develop an model which allows us to rank the relative energy of the **electronic spins and spin states**. The importance of magnetic moments is that the energy of their interactions with a magnetic field can be computed and ranked in terms of a **magnetic energy diagram**, analogous to the electronic state energy diagram for

orbitals (and the vibrational energy diagram for vibrations). Therefore, through the magnetic moments associated with spin through the application of a magnetic field, we will be able to construct magnetic energy diagrams ranking the energy of the various spin orientations corresponding to different states of angular momentum and therefore to different magnetic moments. An important property of such magnetic energy diagrams is that, in contrast to the orbital and vibrational energy diagram, **the separation between the energy levels will depend on the strength of the applied magnetic fields which interact with the electron spin's magnetic moment.**

We have developed quantum intuition concerning the structure and states of electron spins through the use of a vector model allowing the ready visualization of spin angular momentum in a three dimensional vectorial "spin space" and showing how the vectors reside in cones of possible spin orientation. We now need to obtain some physical intuition concerning the energies of these magnetic states from classical mechanics. According to classical mechanics, when a magnetic field is present, each orientation of a given spin state has a different energy. A goal of this Chapter is to provide a means of qualitatively estimating the energies of states in the presence and absence of magnetic fields. We will now use the vector model of spin to associate the spin angular momentum configurations with magnetic moments and magnetic energies in the same way that we associate electronic configurations with electronic energies. We also need to develop a model that will allow us to visualize the interactions and couplings of electron spins leading to **transitions between the magnetic energy levels** corresponding to magnetic resonance spectroscopy and intersystem crossing, which will be the topic of Chapter 3.

2.32 *The Magnetic Moment of an Electron in a Bohr Orbit*

The Bohr model of electrons orbiting about a nucleus provides an exemplar or concrete physical (electron as a particle moving in a circular orbit) model for showing how a magnetic moment (μ) is associated with orbital angular momentum (\mathbf{L}) and spin angular momentum (\mathbf{S}). Through the model of the Bohr atom, we will connect the electron's **orbital angular momentum (\mathbf{L})** with the **magnetic moment (μ_L)** associated with orbital motion. After developing this model, we shall use it as a basis for deducing

the relationship connecting quantum mechanical **spin angular momentum** (\mathbf{S}) and the **magnetic moment** (μ_s) associated with spin motion.

To compute the magnetic motion associated with an electron in a Bohr **orbit**, we first suppose that an electron is a tiny point negative charge rotating at constant velocity in a plane about a fixed axis passing through and perpendicular to the positively charged nucleus (Figure 2.11, left). The orbital motion of an electron of charge $-e$ generates a magnetic field (any charge moving in a circle generates a magnetic field). The magnetic field generated by the orbiting electron may be represented (Fig. 2.11, right) as a *magnetic dipole* (a vector quantity analogous to an electric dipole) with a magnitude proportional to the angular momentum and a direction perpendicular to the plane of the orbit. Analogous to this classical picture by virtue of its constant circular velocity and **orbital** angular momentum, \mathbf{L} , an orbiting Bohr electron generates a fixed magnetic moment, μ_L , that can be represented by a vector coinciding with the axis of rotation (Figure 2.11). This behavior is completely analogous to the classical picture of an electric current flowing in a circular wire, and producing a magnetic moment positioned at the center of the motion and perpendicular to the plane of the wire. The direction of the head of the arrow representing the vector follows the “right hand rule” and points above the plane of rotation for the direction of motion in the orbit shown.

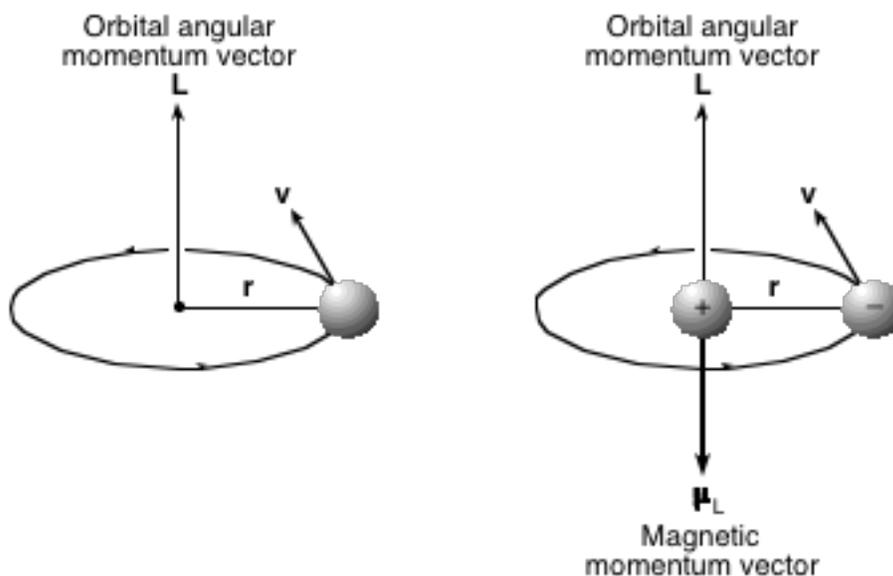


Figure 2.11. *The vector model for the orbital angular momentum and the magnetic moment due to an circular motion of an electron in a Bohr orbit. The direction of the magnetic moment vector is opposite that of the direction of the angular momentum vector for an electron. The units of \mathbf{L} are and the units of $\boldsymbol{\mu}_L$ are $\text{J}\cdot\text{G}^{-1}$.*

From classical physics, the magnetic moment due to orbital motion of the electron, $\boldsymbol{\mu}_L$ is directly proportional to the magnitude of the orbital angular momentum, \mathbf{L} . *This relationship is the important link connecting the value of angular momentum (in general) to the magnetic moment.* From the model of the electron in the Bohr orbit, the proportionality constant between \mathbf{L} and $\boldsymbol{\mu}_L$ can be shown to be $-(e/2m)$, the ratio of the unit of electric charge to the electron's mass, so that a simple relationship exists between the fundamental constants of an electron's charge and mass and the vectors $\boldsymbol{\mu}_L$ and \mathbf{L} as given by Eq. 2.30.

$$\boldsymbol{\mu}_L = -(e/2m)\mathbf{L} \quad (2.30)$$

The proportionality constant $(e/2m)$ reflects a fundamental relationship between the magnetic moment and angular momentum of a Bohr orbit electron and is, therefore, a fundamental quantity of quantum magnetism. This constant is termed the magnetogyric ratio of the electron, and is given a special symbol γ_e . Thus, Eq. 2.30 may be rewritten as Eq. 2.31 (γ_e is defined as a positive quantity).

$$\boldsymbol{\mu}_L = -\gamma_e \mathbf{L} \quad (2.31)$$

If the electron possesses a single unit of angular momentum (\hbar), the magnitude of its magnetic moment, $\boldsymbol{\mu}_L$ is defined as exactly equal to $(e/2m)$. This quantity of magnetism is viewed as the fundamental unit of quantum magnetism for the electron and is given the special name of the Bohr magneton, as well as the special symbol, $\boldsymbol{\mu}_e$. Its numerical value is $9.3 \times 10^{-20} \text{ J}\cdot\text{G}^{-1}$. When we see the symbol $\boldsymbol{\mu}_e$ we can view it as a magnetic moment generated by an electron possessing an angular momentum of exactly 1 \hbar .

The following important concepts can be deduced from Eqs. 2.30 and 2.31:

- (1) The vector representing the magnetic moment, μ_L , and orbital angular momentum, \mathbf{L} , are co-linear (they point in the same direction and are exactly parallel so that they are equivalent vectors related by a proportionality factor, γ_e);
- (2) The vector representing the μ_L is **opposite in direction** to that of \mathbf{L} (the negative sign in Eq. 2.31 relating vectors means that the vectors possess orientations 180° apart);
- (3) The proportionality factor γ_e reveals that the magnitude of the magnetic moment due to orbital motion is directly proportional to the charge of the electron and inversely proportional to its mass.

The reason that Eqs. 2.30 and 2.31 are so important is that they allow us to visualize both the orbital angular momentum, \mathbf{L} , which must be strictly conserved in all magnetic transitions and the magnetic moment, μ_L , which provides the physical interactions determining magnetic energies and "triggering" the occurrence of radiationless and radiative magnetic transitions which will be important for processes involving the intersystem crossing of singlets and triplet states.. Figure 2.11 presents a vectorial description of the relationship of μ_L and \mathbf{L} (the Figure is schematic to the extent that the sizes of the vectors are unitless and not to any particular scale).

Now we need to deduce how a magnetic moment (μ_s) is associated with electron spin angular momentum (\mathbf{S}). We shall start with the quantum results deduced from how the orbital angular momentum (\mathbf{L}) is associated magnetic moment (μ_L) and transfer these ideas to a rotating charged sphere to model electron spin, and then determine what quantum mechanical modifications of the model are necessary to apply our vector model to qualitatively visualize spin.

2.33 *The Magnetic Moment Associated with Electron Spin*

The electron is the lightest quantum particle of chemical interest and, as such, is an exemplar quantum particle and will therefore possess many properties that are quite unusual and unpredictable from observations of classical particles. Nonetheless, there is a clear and appealing visualization that is possible if we start with a model which

considers the electron as a particle of definite mass and spherical shape that possesses a unit negative electric charge distributed uniformly over its surface. The properties of mass and charge are clearly articulated in this simple physical model. In order to understand the angular momentum of the electron resulting from spin motion, it is intuitively natural to assume that since the mass of the electron is fixed and since its spin angular momentum is quantized, and therefore also fixed, the spherical electron must spin about an axis with a fixed velocity, \mathbf{v} (Figure 2.12) in order to obey the fundamental law of conservation of angular momentum. In other words, *because its mass is fixed, and since it must possess a quantum mechanically fixed unit of angular momentum, the velocity of the spinning electron is constant for all electrons.* It is quite straightforward to now apply the results from the Bohr atom relating the orbital angular momentum of an electron to a magnetic moment due to its orbital motion to infer the relationship of the spin angular momentum of an electron to a magnetic moment due to its spin motion.

Analogous to a charged particle executing orbital motion, an electron executing spinning motion also generates a magnetic moment or magnetic dipole. Accordingly, we expect that as a result of its spinning motion, the charged electron will also generate a magnetic moment, $\boldsymbol{\mu}_s$, in analogy to the magnetic moment $\boldsymbol{\mu}_L$ generated by an electron in a circular Bohr orbit. The issue to be addressed is the determination of the relationship between $\boldsymbol{\mu}_s$ and \mathbf{S} .

It is appealing to start with a direct analogy with the relationship of orbital angular momentum, \mathbf{L} , and the associated magnetic moment, $\boldsymbol{\mu}_L$ (Eq. 2.31). An analogy to the latter equation would suggest that the magnitude of the magnetic moment of the spinning electron should be equal to $\gamma_e \mathbf{S}$, i.e., the magnetic moment due to spin should be directly proportional to the value of the spin and the proportionality constant should be γ_e . This simple analogy is of the correct form, but it turns out that experiment shows that the expression is not quantitatively correct. Both experimental evidence and a deeper quantum mechanical theory have shown that although a direct proportionality exists, for a free electron a "correction factor" g_e must be applied to relate $\boldsymbol{\mu}_s$ and \mathbf{S} quantitatively (Eq. 2.32).

$$\boldsymbol{\mu}_s = -g_e \gamma_e \mathbf{S} \quad (2.32)$$

In Eq. 2.32, g_e is a dimensionless constant called the g factor (or g value) of the free electron and has an experimental value of close to 2. Thus, the simple model which attempts to transfer the properties of an orbiting electron to a spinning electron is correct in qualitative form, but is incorrect by a factor of 2. This factor of 2 is fully justified in a more rigorous theory of the electron which considers relativistic effects, but this rather subtle issue is not of concern for the qualitative features of spin of interest in this text.

Figure 2.12 uses the vector model to summarize the relationships between the spin angular momentum and the magnetic moment associated with electron spin. Figure 2.12 should be compared to the analogous form of the orbital angular momentum and its associated magnetic moment in Figure 2.11.

From Eq. 2.32 and Fig. 2.12, the following important conclusions can be made concerning the relationship between electron spin and the magnetic moment due to spin:

- (1) Since spin is quantized and the spin vector and the magnetic moment vectors are directly related: **the magnetic moment associated with spin (μ_s), as the angular momentum (S) from which it arises, is quantized in magnitude and orientation;**
- (2) Since the energy of a magnetic moment depends on its orientation in a magnetic field, **the energies of various quantized spin states will depend on the orientation of the spin vector in a magnetic field;**
- (3) In analogy to the relationship of the orbital angular momentum and the magnetic moment derived from orbital motion, the vectors μ_s and S are antiparallel (Figure 2.12, left);
- (4) The vectors μ_s and S are both positioned in a cone of orientation which depends on the value of M_S (Figure 2.12, right).

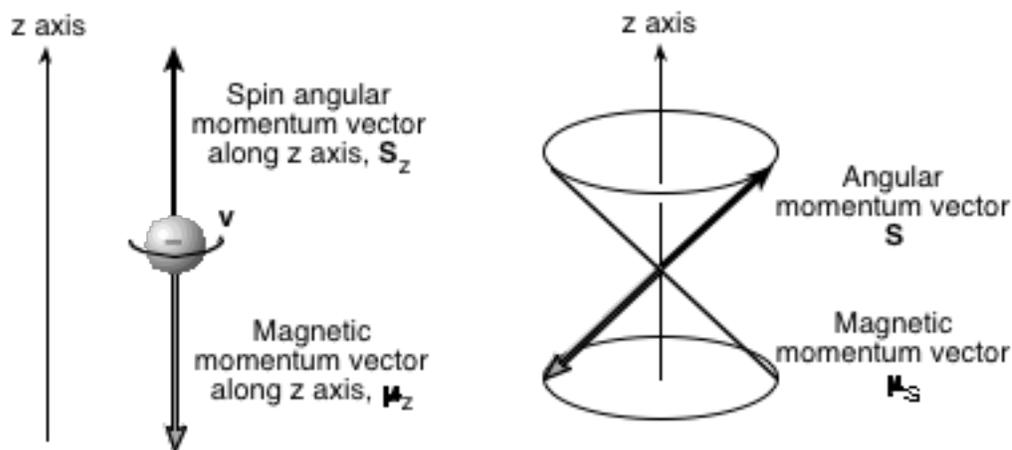


Figure 2.12. *Vector representation of the spin angular momentum, S , and the magnetic moment associated with spin, μ_S . The two vectors are collinear, but antiparallel.*

2.34 Classical Magnetic Energy Levels in an Applied Magnetic Field

We have now developed a model that allows the association of a specific value of a magnetic moment with specific value of spin angular momentum. Our next goal is to develop a model for the magnetic energy levels associated with different values of spin for electrons in a magnetic field. Let us consider what happens to the magnetic energy levels when a magnetic field is applied. As has been our protocol, we shall examine the results for an exemplar classical magnet and then apply these results to determine how the quantum magnet associated with the electron spin changes its energy when it couples with any applied magnetic field. The vector model not only provides an effective tool to deal with the qualitative and quantitative aspects of the magnetic energy levels, but will also provide us with an excellent tool for visualizing the qualitative and quantitative aspects of transitions between magnetic energy levels discussed in Chapter 3.

According to classical physics, a magnetic field is characterized by a magnetic moment, which is a vector quantity and given the symbol \mathbf{H}_0 . When a bar magnet possessing a magnetic moment $\boldsymbol{\mu}$, is placed in a magnetic field, \mathbf{H}_0 , a torque operates on the magnetic moment of the bar magnet and twists it with a force that tries to align the direction of the moment with the direction of the field determined by \mathbf{H}_0 . The precise

equation describing the energy relationship of the bar magnetic at various orientations in \mathbf{H}_0 is given by equation 2.31, where μ and \mathbf{H}_z are the magnitudes of the magnetic moments of the bar magnet and the applied field in the z direction, respectively. According to classical mechanics, any orientation of the bar magnet in the magnetic field is possible. Three important limiting orientations, parallel (0°), antiparallel (180°) and perpendicular (90°), of bar magnetic relative to the magnetic field are shown schematically in Figure 2.13.

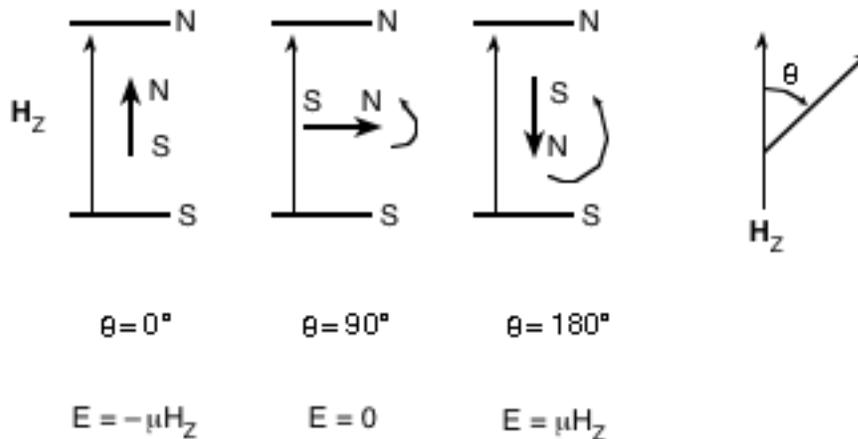


Figure 2.13. *Energies of a classical bar magnet in a magnet field, H_0 . The curved arrow indicates the force acting to rotate the magnet to align it with the direction of the field.*

$$E \text{ (magnetic)} = -\mu H_z \cos\theta \quad (2.33)$$

In Eq. 2.33 the negative sign before the quantity on the right side of the equation means that the system becomes more stable if the product of $mH_z \cos\theta$ is a positive quantity. By definition, the magnitudes (lengths) of the vector quantities μ and \mathbf{H}_z are always positive. So, whether the energy of the system is positive (less stable than the situation in zero field) or negative (more stable than the situation in zero field) depends on the sign of $\cos\theta$ (which is positive for θ between 0° and 90° and negative for θ between 90° and 180°).

Let us consider the situation when $\boldsymbol{\mu}$ and \mathbf{H}_z are two parallel vectors ($\theta = 0$), two perpendicular vectors ($\theta = 90^\circ$ or $\pi/2$), or two antiparallel vectors ($\theta = 180^\circ$ or π). For these cases, $\cos\theta = 1, 0$ and -1 , respectively (Figure 2.13). We can make the important conclusions that any orientation of the bar magnet with θ between 0 and less than 90° is stabilizing (the E in Eq. 2.31 is negative relative to the zero of magnetic energy) and any orientation of the bar magnet with θ between 90° and up to 180° is destabilizing (the E in Eq. 2.31 is positive relative to the zero of magnetic energy). Importantly, at an orientation of 90° the magnetic interactions between the applied magnetic field and the bar magnet are zero ($\cos 90^\circ = 0$), i.e., the same as they are in the absence of a field!

2.35 *Quantum Magnets in the Absence of Coupled Magnetic Fields*

We take the classical model for a bar magnetic in a magnetic field and develop a model for a “quantum magnet” due to electron spin in a magnetic field. We shall concentrate on the three most important spin situations that are encountered in molecular organic photochemistry: a single electron spin (which is found for free organic radicals) and two coupled spins (which is found for singlet and triplet states).

We establish a convention that will be a convenient form to discuss the important spin situations of a single spin and two coupled spins. Table 3 summarizes the notations and vector representations for a single spin and two coupled spins and will be used to describe spin systems at both zero and high applied magnetic fields. We use the symbol D (doublet) to describe the state of a single spin. For the case of $M_S = +1/2$ (α or up spin), we label the state D_+ ; and for the case of $M_S = 1/2$ (β or down spin), we label the state D_- . In the case of two coupled spins we use the symbol S to denote the singlet state (one α spin and one β spin, wavefunction = $\alpha\beta + \beta\alpha$). This state has the quantum number $M_S = 0$. For the triplet state we use the symbols T_+ (two α spins), T_0 (one α spin and one β spin, wavefunction = $\alpha\beta + \beta\alpha$) and T_- (two β spins) to label the states with quantum numbers of $M_S = +1, 0, -1$, respectively. We have noted in Section 2.26 that both the S and T_0 states possess one α spin and one β spin and a quantum number of $M_S = 0$ and appear to be equivalent. We shall address and remedy this situation below.

In the absence of magnetic interactions operating on the magnetic moments associated with electron spins, all of the five states (D , S , T_{-} , T_0 , T_{+}) have exactly the same energy, i.e., the magnetic energy levels of all of these states are all degenerate. In the absence of any magnetic interactions, the vector model of a single electron spin views the vector representing the angular momentum and magnetic moment as stationary and possessing random orientations in space. There is no pertinent M_S quantum number in for zero field, because there is **no preferred** axis of orientation. However, even at zero field the total spin angular momentum ($S = 0, 1/2, 1$) is well defined, so we say that the quantum number for total spin is still a good quantum number. In other words, a D or T state is magnetic and a S state is non-magnetic whether or not an applied field is present.

2.36 Constructing a Magnetic Energy Diagram. Quantum Magnetic Energy Levels in a Strong Applied Field. Zeeman Magnetic Energies

The magnetic energy of interaction of a magnetic moment and an applied field (Figure 2.13) is known as the **Zeeman energy**. Eq. 2.32 relates the magnetic moment of the quantum magnet due to electron spin with the value of the g factor, the strength of the magnetic field and the value of the spin angular momentum. Eq. 2.34 relates the energy of the quantum magnet to the strength of the applied field, H_0 , the magnetic quantum number for a given spin orientation, M_S , the g -value of the electron and the universal constant μ_e , the magnetic moment of a free electron.

$$E = M_S g \mu_e H Z \tag{2.34}$$

Thus, the ranking of magnetic energies (relative to those in zero field) of the singlet, doublet and triplet states are readily computed and are shown in Table 3.

State	State Symbol	M_S	Magnetic Energy	Spin Function	Vector Representation
Doublet	D_+	$+1/2$	$+(1/2)g\mu_e H_Z$	α	
Doublet	D_-	$-1/2$	$-(1/2)g\mu_e H_Z$	β	
Singlet	S	0	0	$\alpha\beta - \beta\alpha$	
Triplet	T_+	$+1$	$+(1)g\mu_e H_Z$	$\alpha\beta + \beta\alpha$	
Triplet	T_0	0	0	$\alpha\beta + \beta\alpha$	
Triplet	T_-	-1	$-(1)g\mu_e H_Z$	$\alpha\beta + \beta\alpha$	

Table 3. Conventional representations of singlet, doublet and triplet states in an applied magnetic field H_Z . A mathematical normalizing factor is not shown for the spin function.

2.37 Magnetic Energy Diagram for A Single Electron Spin and Two Coupled Electron Spins

Figure 2.14 displays the magnetic energy level diagram at zero magnetic field and in the presence of a magnetic field for the two fundamental cases of : (1) a single electron spin, a doublet or D state and (2) two correlated electron spins, which may be either a triplet, T, or singlet, S state. In zero field (ignoring the electron exchange interaction, J , and only considering the magnetic interactions) all of the magnetic energy levels are degenerate, because there is no preferred orientation of the angular momentum and therefore no preferred orientation of the magnetic moment due to spin. Although these states are all of the same energy, they are shown with levels slightly separated so that the number of degenerate states is clear. Remember that these states have identical energies in the absence of magnetic interactions.

The zero field situation is a point of calibration of magnetic coupling energy in devising a magnetic energy diagram. The concept is the same as using the energy of a non-bonding p orbital as a zero of energy and then to consider bonding orbitals as lower in energy than a p orbital, and anti-bonding orbitals as higher in energy than a p orbital. The magnitude of the exchange interaction (Section 2.7) is typically much larger than magnetic interactions. However, the exchange interaction is a Coulombic (electrostatic) interaction and is not magnetic. This allows us to consider the magnetic interactions first and independently, as shown in Figure 2.14, and to later "turn on" the electrostatic interactions after considering the magnetic interactions.

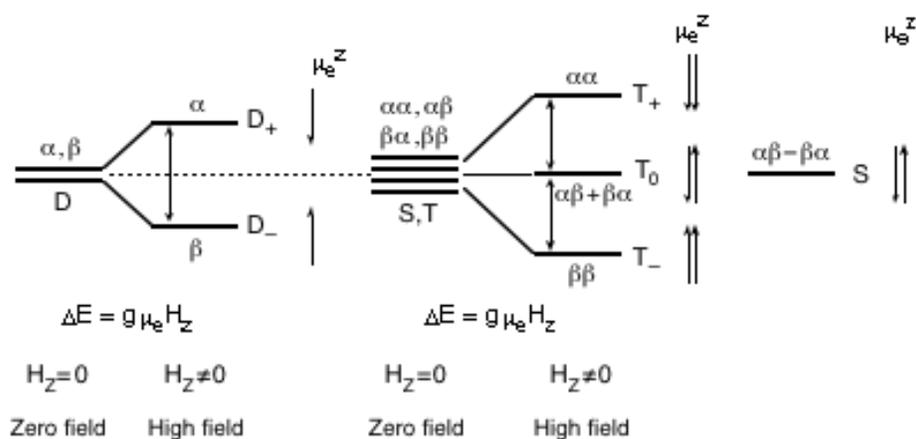


Figure 2.14. *Magnetic energy diagram for a single electron spin and two correlated electron spins.*

2.38 Magnetic Energy Diagrams Including the Electron Exchange Interaction

As mentioned above, the exchange interaction, J , between two electrons results in a quantum mechanical electrostatic (non-magnetic) splitting of the energy of the singlet state from the triplet states (Section 2.7). As a result, the energy diagrams shown in Figure 2.14 must be modified in the presence of electron exchange. First we need to comment on a significant difference between the situation for singlet-triplet splittings for molecules (*R and R) and for reactive intermediates (I). Consider a radical pair for which a single bond has been stretched and broken as an example of I. Fig. 2.6 is an exemplar potential energy curve for such a situation. Near the minimum of the curve the electron exchange is strong in both R and *R because the molecular orbitals of X and Y are close together (r_{xy} ca 0.7 Å) and strongly overlapping. When the bond is stretched to ca 3 Å the bond is essentially broken. At this point overlap between the orbitals of X and Y is small. Since the value of the overlap integral, J , falls off rapidly as a function of distance, there is relatively little electron exchange in the region of separation near and beyond values of separation of ca 3 Å and larger. In the case discussed in Section 2.7, the singlet and triplet states being compared were S_1 and T_1 , both derived from a HO-LU orbital configuration corresponding to *R. Even in the case of *R = n, π^* the value of the exchange integral is of the order of several kcal/mol or greater.

Let us use the term T and S for the triplet state and the singlet state of I. For a radical pair the value of J can be of the order of 10^{-3} kcal/mol. Such weak exchange interactions have two important consequences: (1) the magnitude of the exchange forces between electrons become of the same order of magnitude as the magnetic forces between electrons for I; (2) T no longer is lower in energy than the S for I. The reason for (1) is straightforward and has to do with the fall off of J and the magnetic forces with separation of X and Y. The reason for (2) is a bit more subtle, but is also straightforward if we consider that for large separations (infinity) of X and Y which correspond to $J = 0$, the singlet and triplet have the same energy! This is the same situation that would exist if the electrons in molecules did not correlate with one another. So as X and Y move closer together, what happens to the relative energies of the two states? Clearly the S_0 state is always lower than the T_1 state, so it would not be surprising if for I the S state was lower in energy than the T state. The reason that the S state drops in energy is that the two electrons with paired spins correlate with S_0 which does not possess an antibonding electron. T on the other hand must correlate with T_1 , which does possess an antibonding electron. When comparing $^*R(S_1)$ with $^*R(T_1)$ **both states possess an antibonding electron**. In summary, the value of J for radical pairs will be small and the S state of a radical pair will generally be lower in energy than that of the triplet state, T. In these cases the electron exchange effectively stabilizes the system by contributing to bonding in addition to repulsions when the two electrons are together in the singlet state. When the orbitals which contain the two electrons of interest are involved in orbitals for which bonding is substantial, J becomes a negative energy term and makes the electron spin pairing situation (singlet) more stable than the spin unpairing situation (triplet).

There are three limiting situations for which the combination of exchange and magnetic field effects are important in photochemical systems.

For case I one $J = 0$ and $H_0 = 0$ (Figure 2.15, left). In Case I although S and T are distinct states, they are degenerate in energy. Importantly, the three sublevels of T (T_+ , T_0 and T_-) are degenerate (same energy) and can be viewed as rapidly interconverting along the molecular axis as the molecule tumbles and rotates in solution. This situation may be considered in analogy to three rapidly equilibrating conformers of identical

energy and structure. We shall see that Case I is typical of situations for which there is no magnetic field present and the two spins are separated by large distances ($>3\text{-}5 \text{ \AA}$) in space and as is the case for solvent-separated, spin-correlated geminate pairs and long biradicals.

Case II is one for which $H_0 = 0$, but for which there is a finite value, but small value of J , comparable to the value of the magnetic interactions between the electron spins. Case II is typical of situations for which the two spins are close enough together so that their orbitals overlap slightly in space as is the case for spin correlated radical pairs and small biradicals. Case III is one for which a high field, H_0 , is present and for which the values of J are 0 or are comparable to the Zeeman splitting (i.e., $J = 0$ or $J \sim g\mu_e H$). In this special case, the T_{\pm} and S state may have comparable energies. This situation is important as we shall see in Chapter 3, because closeness in energy sets up favorable conditions for transitions between states. In other words, when T_{\pm} and S are very close in energy, the conditions are favorable for $T_{\pm} \rightarrow S$ and $S \rightarrow T_{\pm}$ intersystem crossings in I.

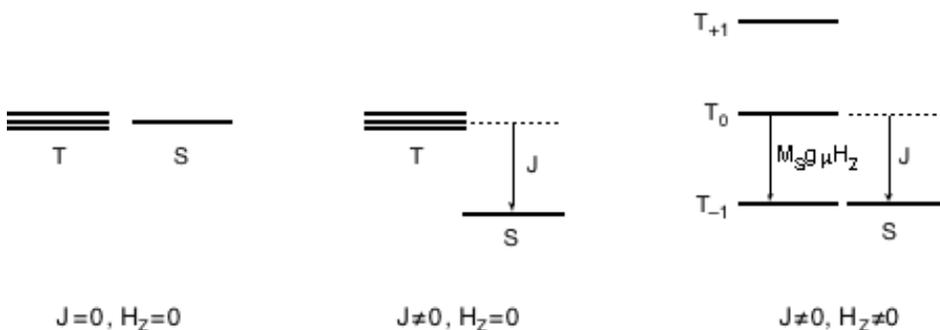


Figure 2.15 *Effect of electron exchange on the magnetic energy levels of a triplet and singlet state. See text for discussion*

2.39 Interactions between Two Magnetic Dipoles. *Orientational and Distance Dependence of the Energy of Magnetic Interactions*

A magnetic moment is a magnetic dipole, i.e., the magnetic moment gives rise to a magnetic field in its vicinity Fig. 2.16. We shall investigate the mathematical form of the two interactions in order to obtain some intuition concerning the magnitude of the

interactions as a function of spin structure and orientation of spins in space. Fig. 2.16 shows one of the line of force which emanate from a magnetic dipole (the same picture, importantly, holds for electric dipoles). The lines of force can be traced as leaving and then reentering the vicinity of the dipole. The “direction” of the magnetic force varies as a function of the space about the dipole. For example, in regions 1 and 3 the lines of force are in the same direction as that of the dipole moment. However, in region 2 the lines of force are in an opposite direction to that of the dipole moment. Clearly the degree of interaction between two dipoles will depend on their relative orientation to one another.

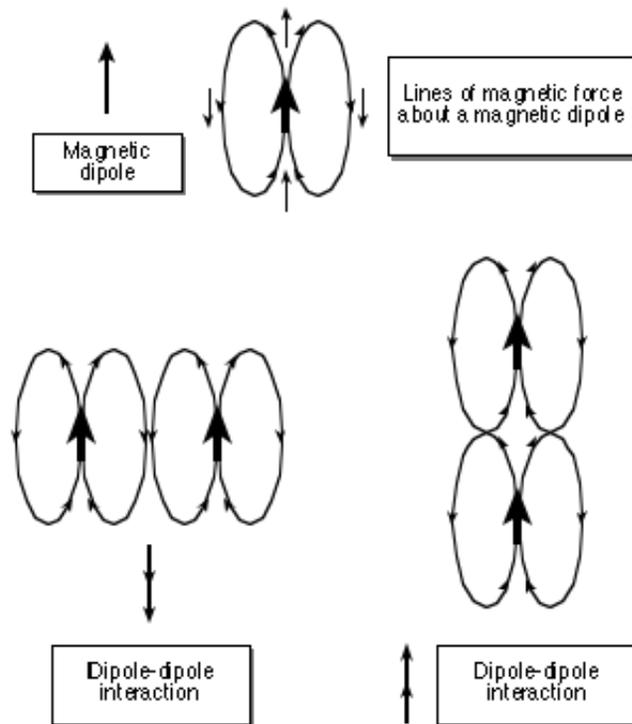


Figure 2.16. (a) A dipole (magnetic or electric); (b) one line of force the force field in the vicinity of a dipole; (c) a dipole-dipole interaction with parallel dipoles at an angle of 90° to one another; (d) a dipole-dipole interaction with parallel dipoles at an angle of 0° to one another.

Insight to the nature of the magnetic dipole-dipole interaction is available from consideration of the mathematical formulation of the interaction and its interpretation in terms of the vector model. The beauty of the formulation is that its representation provides an identical basis to consider all forms of dipole-dipole interactions. These may be due to electric dipoles interacting (two electric dipoles, an electric dipole and a nuclear

dipole or two nuclear dipoles) or to magnetic dipoles interacting (two electron spins, an electron spin and a nuclear spin, two nuclear spins, a spin and a magnetic field, a spin and an orbital magnetic dipole, etc.).

Classically, the dipole-dipole interaction energy depends on the relative orientation of the magnetic moments (consider two bar magnets). To obtain some concrete insight to the dipolar interaction consider the case for which the two magnetic dipoles, μ_1 and μ_2 , are held parallel to one another (this is the case for two interacting magnetic dipoles in a strong magnetic field (Fig. 2.18). We can obtain an intuitive feeling for the nature of the dipole-dipole interaction by considering the terms of the dipole-dipole interaction in Eq. 2.35. In general, the strength of the interaction is proportional to several factors: (1) the magnitudes of the individual interacting dipoles; (2) the distance separating the interacting dipoles; (3) the angles of orientation of the dipoles relative to one another; and (4) the "spectral overlap" of resonances that satisfy the conservation of angular momentum and energy. In fact, Eq. 2.33 strictly speaking refers to the interaction of two "point" dipoles (if r , the separation between the dipoles is large relative to the dipole length, the dipole may be considered a "point" dipole).

$$\text{Dipole-dipole interaction} \propto [(\mu_1\mu_2)/r^3](3\cos^2\theta - 1)(\text{overlap integral}) \quad (2.35)$$

For dipole-dipole interactions in solution, the rate of processes involving dipole-dipole interactions is typically proportional to the **square** of the strength of the dipole-dipole interaction. Thus, the field strength falls off as $1/r^3$, but the rate of a process driven by dipolar interactions falls off as $1/r^6$.

The term involving the $3\cos^2\theta - 1$ (Fig. 2.17) is particularly important because of two of its features: (1) for a fixed value of r and interacting magnetic moments, this term causes the interaction energy to be highly dependent on the angle θ that the vector r makes with the z axis and (2) the value of this term averages to zero if all angles are represented, i.e., the average value of $\cos^2\theta$ over all space is $1/3$. A plot of $y = 3\cos^2\theta - 1$ is shown at the bottom of Figure 2.17. It is seen that the values of y are symmetrical

about $\theta = 90^\circ$. It is interesting to note that for values of $\theta = 54^\circ$ and 144° , the value of $y = 0$, i.e., for these particular angles, the dipolar interaction disappears even when the

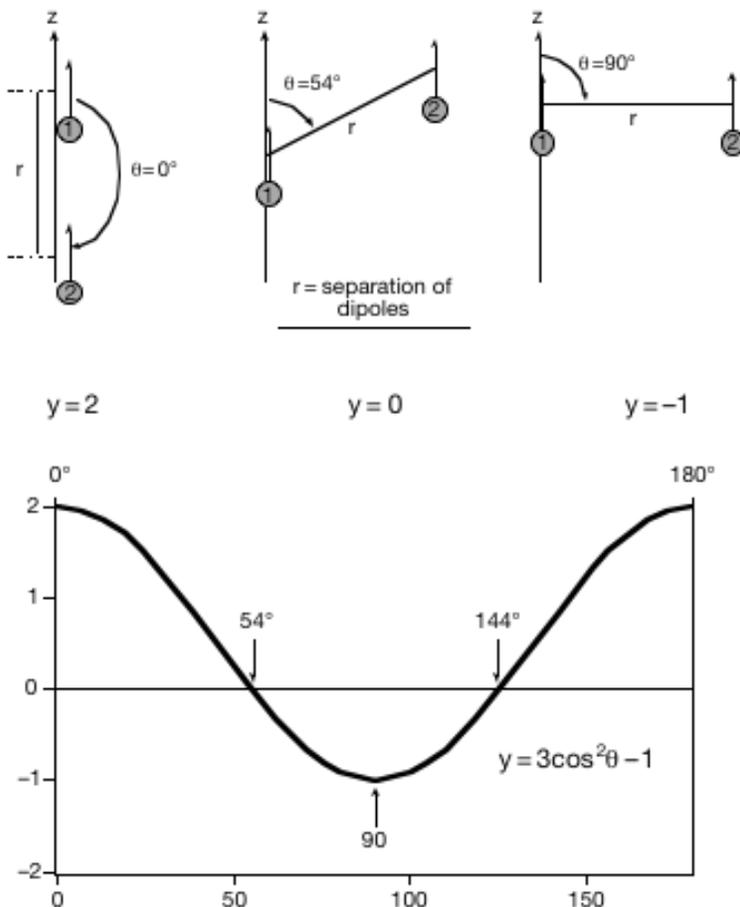


Figure 2.17. Dipole-dipole interactions of parallel magnetic moments. Top: vector representation of dipoles interacting at a fixed separation, r , and various orientations relative to a z axis. Bottom: plot of the value of $3\cos^2\theta - 1$ as a function of θ .

spins are close in space! This is the familiar "magic angle" employed to spin samples in the magnetic field of an NMR spectrometer for removing chemical shifts due to dipolar interactions. It is important to note that certain values of y are positive (magnetic energy raising) and certain values of y are negative (magnetic energy decreasing).

2.39 Summary

We have developed working paradigms for describing the structure and energetics of electron spin employing a vector model of spin and relating it to magnetic moments. In Chapter 3 we shall consider the dynamics of spin that are critical in processes which interconvert spin states, in particular the *intersystem crossing* between spin states involved in singlet triplet interconversions and triplet singlet interconversions.

Although understanding and use of the paradigm of quantum mechanics requires a sophisticated mathematical background, in this chapter we have attempted to describe and picture the wave functions of electrons, spins and vibrations may be approximated by pictorial representations that are useful for understanding the qualitative aspects of organic photochemistry. In this chapter we have considered the visualization of the electronic, spin and vibrational structure of the starting points for photochemical reactions, R^* . In Chapter 3 we will consider the visualization of the photophysical and photochemical transitions of R^* .