Section 3 Electronic Configurations, Term Symbols, and States

Introductory Remarks- The Orbital, Configuration, and State Pictures of Electronic Structure

One of the goals of quantum chemistry is to allow practicing chemists to use knowledge of the electronic states of fragments (atoms, radicals, ions, or molecules) to predict and understand the behavior (i.e., electronic energy levels, geometries, and reactivities) of larger molecules. In the preceding Section, orbital correlation diagrams were introduced to connect the orbitals of the fragments along a 'reaction path' leading to the orbitals of the products. In this Section, analogous connections are made among the fragment and product electronic states, again labeled by appropriate symmetries. To realize such connections, one must first write down N-electron wavefunctions that possess the appropriate symmetry; this task requires combining symmetries of the occupied orbitals to obtain the symmetries of the resulting states.

Chapter 8
Electrons are Placed into Orbitals to Form Configurations, Each of Which Can be Labeled by its Symmetry. The Configurations May "Interact" Strongly if They Have Similar Energies.

I. Orbitals Do Not Provide the Complete Picture; Their Occupancy By the N Electrons Must Be Specified

Knowing the orbitals of a particular species provides one information about the sizes, shapes, directions, symmetries, and energies of those regions of space that are available to the electrons (i.e., the complete set of orbitals that are available). This knowledge does not determine into which orbitals the electrons are placed. It is by describing the electronic configurations (i.e., orbital occupancies such as $1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p^1 3s^1$) appropriate to the energy range under study that one focuses on how the electrons occupy the orbitals. Moreover, a given configuration may give rise to several energy levels whose energies differ by chemically important amounts. for example, the $1s^2 2s^2 2p^2$ configuration of the Carbon atom produces nine degenerate ^3P states, five degenerate ^1D states, and a single ^1S state. These three energy levels differ in energy by 1.5 eV and 1.2 eV, respectively.

II. Even N-Electron Configurations Are Not Mother Nature's True Energy States

Moreover, even single-configuration descriptions of atomic and molecular structure (e.g., $1s^2 2s^2 2p^4$ for the Oxygen atom) do not provide fully correct or highly accurate representations of the respective electronic wavefunctions. As will be shown in this Section and in more detail in Section 6, the picture of N electrons occupying orbitals to form a configuration is based on a so-called "mean field" description of the coulomb interactions among electrons. In such models, an electron at $\mathbf{r}$ is viewed as interacting with an "averaged" charge density arising from the N-1 remaining electrons:

$$V_{mean\ field} = \quad _{N-1}(\mathbf{r'})\ e^2/|\mathbf{r-r'}|\ \mathbf{dr'} \quad .$$

Here $_{N-1}(\mathbf{r'})$ represents the probability density for finding electrons at $\mathbf{r'}$, and $e^2/|\mathbf{r-r'}|$ is the mutual coulomb repulsion between electron density at $\mathbf{r}$ and $\mathbf{r'}$. Analogous mean-field models arise in many areas of chemistry and physics, including electrolyte theory (e.g., the Debye-Hückel theory), statistical mechanics of dense gases (e.g., where the Mayer-Mayer cluster expansion is used to improve the ideal-gas mean field model), and chemical dynamics (e.g., the vibrationally averaged potential of interaction).

In each case, the mean-field model forms only a starting point from which one attempts to build a fully correct theory by effecting systematic corrections (e.g., using perturbation theory) to the mean-field model. The ultimate value of any particular mean-field model is related to its accuracy in describing experimental phenomena. If predictions of the mean-field model are far from the experimental observations, then higher-order corrections (which are usually difficult to implement) must be employed to improve its predictions. In such a case, one is motivated to search for a better model to use as a starting point so that lower-order perturbative (or other) corrections can be used to achieve chemical accuracy (e.g., ± 1 kcal/mole).

In electronic structure theory, the single-configuration picture (e.g., the $1s^2 2s^2 2p^4$ description of the Oxygen atom) forms the mean-field starting point; the configuration interaction (CI) or perturbation theory techniques are then used to systematically improve this level of description.

The single-configuration mean-field theories of electronic structure neglect correlations among the electrons. That is, in expressing the interaction of an electron at $\mathbf{r}$

with the N-1 other electrons, they use a probability density $_{N-1}(\mathbf{r'})$ that is independent of the fact that another electron resides at $\mathbf{r}$. In fact, the so-called conditional probability density for finding one of N-1 electrons at $\mathbf{r'}$, given that an electron is at $\mathbf{r}$ certainly depends on $\mathbf{r}$. As a result, the mean-field coulomb potential felt by a $2p_x$ orbital's electron in the $1s^2 2s^2 2p_x 2p_y$ single-configuration description of the Carbon atom is:

$$V_{\text{mean field}} = 2 \int |1s(\mathbf{r'})|^2 \ e^2/|\mathbf{r}\text{-}\mathbf{r'}| \ \mathbf{dr'}$$

$$+ \ 2 \int |2s(\mathbf{r'})|^2 \ e^2/|\mathbf{r}\text{-}\mathbf{r'}| \ \mathbf{dr'}$$

$$+ \ \int |2p_y(\mathbf{r'})|^2 \ e^2/|\mathbf{r}\text{-}\mathbf{r'}| \ \mathbf{dr'} \ .$$

In this example, the density $_{N-1}(\mathbf{r'})$ is the sum of the charge densities of the orbitals occupied by the five other electrons
$2 |1s(\mathbf{r'})|^2 + 2 |2s(\mathbf{r'})|^2 + |2p_y(\mathbf{r'})|^2$, and is not dependent on the fact that an electron resides at $\mathbf{r}$.

III. Mean-Field Models

The Mean-Field Model, Which Forms the Basis of Chemists' Pictures of Electronic Structure of Molecules, Is Not Very Accurate

The magnitude and "shape" of such a mean-field potential is shown below for the Beryllium atom. In this figure, the nucleus is at the origin, and one electron is placed at a distance from the nucleus equal to the maximum of the 1s orbital's radial probability density (near 0.13 Å). The radial coordinate of the second is plotted as the abscissa; this second electron is arbitrarily constrained to lie on the line connecting the nucleus and the first electron (along this direction, the inter-electronic interactions are largest). On the ordinate, there are two quantities plotted: (i) the Self-Consistent Field (SCF) mean-field potential $\int |1s(\mathbf{r'})|^2 \ e^2/|\mathbf{r}\text{-}\mathbf{r'}| \ \mathbf{dr'}$, and (ii) the so-called Fluctuation potential (F), which is the true coulombic $e^2/|\mathbf{r}\text{-}\mathbf{r'}|$ interaction potential minus the SCF potential.
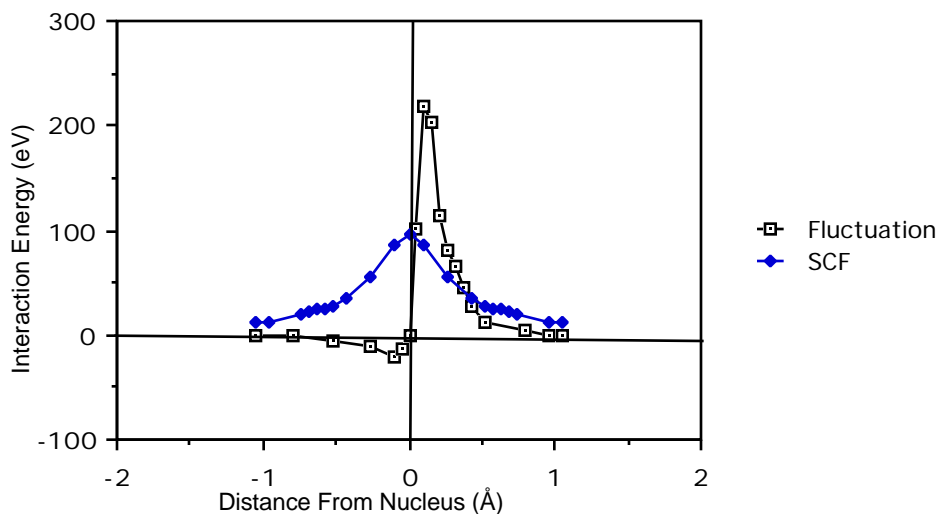
As a function of the inter-electron distance, the fluctuation potential decays to zero more rapidly than does the SCF potential. For this reason, approaches in which F is treated as a perturbation and corrections to the mean-field picture are computed perturbatively might be expected to be rapidly convergent (whenever perturbations describing long-range interactions arise, convergence of perturbation theory is expected to be slow or not successful). However, the magnitude of F is quite large and remains so over an appreciable range of inter-electron distances.

The resultant corrections to the SCF picture are therefore quite large when measured in kcal/mole. For example, the differences ∆E between the true (state-of-the-art quantum chemical calculation) energies of interaction among the four electrons in Be and the SCF mean-field estimates of these interactions are given in the table shown below in eV (recall that 1 eV = 23.06 kcal/mole).

Orb. Pair	1s 1s	1s 2s	1s 2s	1s 2s	1s 2s	2s 2s
∆E in eV	1.126	0.022	0.058	0.058	0.022	1.234

To provide further insight why the SCF mean-field model in electronic structure theory is of limited accuracy, it can be noted that the average value of the kinetic energy plus the attraction to the Be nucleus plus the SCF interaction potential for one of the 2s orbitals of Be with the three remaining electrons in the $1s^2 2s^2$ configuration is:

$$< 2s| -\hbar^2/2m_e \nabla^2 - 4e^2/r + V_{SCF} |2s> = -15.4 \text{ eV};$$

the analogous quantity for the 2p orbital in the $1s^2 2s 2p$ configuration is:

$$< 2p| -\hbar^2/2m_e \nabla^2 - 4e^2/r + V'_{SCF} |2p> = -12.28 \text{ eV};$$

the corresponding value for the 1s orbital is (negative and) of even larger magnitude. The SCF average coulomb interaction between the two 2s orbitals of $1s^2 2s^2$ Be is:

$$\int |2s(\mathbf{r})|^2 |2s(\mathbf{r'})|^2 e^2/|\mathbf{r}-\mathbf{r'}| \, \mathbf{dr} \, \mathbf{dr'} = 5.95 \text{ eV}.$$

This data clearly shows that corrections to the SCF model (see the above table) represent significant fractions of the inter-electron interaction energies (e.g., 1.234 eV compared to 5.95- 1.234 = 4.72 eV for the two 2s electrons of Be), and that the inter-electron interaction energies, in turn, constitute significant fractions of the total energy of each orbital (e.g., 5.95 -1.234 eV = 4.72 eV out of -15.4 eV for a 2s orbital of Be).

The task of describing the electronic states of atoms and molecules from first principles and in a chemically accurate manner (± 1 kcal/mole) is clearly quite formidable. The orbital picture and its accompanying SCF potential take care of "most" of the interactions among the N electrons (which interact via long-range coulomb forces and whose dynamics requires the application of quantum physics and permutational symmetry). However, the residual fluctuation potential, although of shorter range than the bare coulomb potential, is large enough to cause significant corrections to the mean-field picture. This, in turn, necessitates the use of more sophisticated and computationally taxing techniques (e.g., high order perturbation theory or large variational expansion spaces) to reach the desired chemical accuracy.

Mean-field models are obviously approximations whose accuracy must be determined so scientists can know to what degree they can be "trusted". For electronic structures of atoms and molecules, they require quite substantial corrections to bring them into line with experimental fact. Electrons in atoms and molecules undergo dynamical motions in which their coulomb repulsions cause them to "avoid" one another at every instant of time, not only in the average-repulsion manner that the mean-field models embody. The inclusion of instantaneous spatial correlations among electrons is necessary to achieve a more accurate description of atomic and molecular electronic structure.

IV. Configuration Interaction (CI) Describes the Correct Electronic States

The most commonly employed tool for introducing such spatial correlations into electronic wavefunctions is called configuration interaction (CI); this approach is described briefly later in this Section and in considerable detail in Section 6.

Briefly, one employs the (in principle, complete as shown by P. O. Löwdin, Rev. Mod. Phys. 32, 328 (1960)) set of N-electron configurations that (i) can be formed by placing the N electrons into orbitals of the atom or molecule under study, and that (ii) possess the spatial, spin, and angular momentum symmetry of the electronic state of interest. This set of functions is then used, in a linear variational function, to achieve, via the CI technique, a more accurate and dynamically correct description of the electronic structure of that state. For example, to describe the ground ^1S state of the Be atom, the $1s^22s^2$ configuration (which yields the mean-field description) is augmented by including other configurations such as $1s^23s^2$, $1s^22p^2$, $1s^23p^2$, $1s^22s3s$, $3s^22s^2$, $2p^22s^2$, etc., all of which have overall ^1S spin and angular momentum symmetry. The excited ^1S states are also combinations of all such configurations. Of course, the ground-state wavefunction is dominated by the $|1s^22s^2|$ and excited states contain dominant contributions from $|1s^22s3s|$, etc. configurations. The resultant CI wavefunctions are formed as shown in Section 6 as linear combinations of all such configurations.

To clarify the physical significance of mixing such configurations, it is useful to consider what are found to be the two most important such configurations for the ground ^1S state of the Be atom:

$$C_1 \, |1s^22s^2| - C_2 \, [|1s^22p_x^2| + |1s^22p_y^2| + |1s^22p_z^2 \, |].$$

As proven in Chapter 13.III, this two-configuration description of Be's electronic structure is equivalent to a description is which two electrons reside in the 1s orbital (with opposite, and   spins) while the other pair reside in 2s-2p hybrid orbitals (more correctly, polarized orbitals) in a manner that instantaneously correlates their motions:

$$1/6 \, C_1 \, |1s^2\{[(2s\text{-}a2p_x) \; (2s\text{+}a2p_x) \; - (2s\text{-}a2p_x) \; (2s\text{+}a2p_x) \;]$$

$$+[(2s\text{-}a2p_y) \; (2s\text{+}a2p_y) \; - (2s\text{-}a2p_y) \; (2s\text{+}a2p_y) \;]$$

$$+[(2s\text{-}a2p_z) \; (2s\text{+}a2p_z) \; - (2s\text{-}a2p_z) \; (2s\text{+}a2p_z) \;]\}|,$$

where $a = \sqrt{3C_2/C_1}$. The so-called polarized orbital pairs
$(2s \pm a \, 2p_{x,y, \text{ or } z})$ are formed by mixing into the 2s orbital an amount of the $2p_{x,y, \text{ or } z}$ orbital, with the mixing amplitude determined by the ratio of C_2 to C_1 . As will be detailed in Section 6, this ratio is proportional to the magnitude of the coupling $<|1s^2 2s^2 |H|1s^2 2p^2| >$ between the two configurations and inversely proportional to the energy difference $[<|1s^2 2s^2|H|1s^2 2s^2|> - <|1s^2 2p^2|H|1s^2 2p^2|>]$ for these configurations. So, in general, configurations that have similar energies (Hamiltonian expectation values) and couple strongly give rise to strongly mixed polarized orbital pairs. The result of forming such polarized orbital pairs are described pictorially below.

$2s - a \, 2p_z$
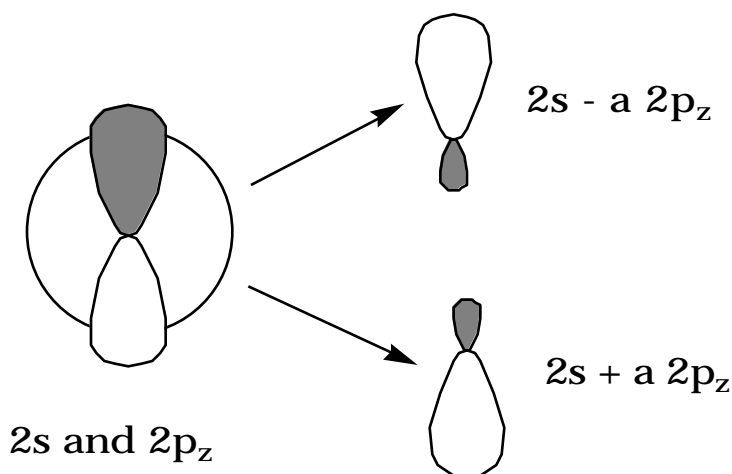
$2s + a \, 2p_z$

$2s$ and $2p_z$

Polarized Orbital 2s and 2p $_z$ Pairs

In each of the three equivalent terms in this wavefunction, one of the valence electrons moves in a 2s+a2p orbital polarized in one direction while the other valence electron moves in the 2s-a2p orbital polarized in the opposite direction. For example, the first term $[(2s-a2p_x) \ (2s+a2p_x) \ - (2s-a2p_x) \ (2s+a2p_x) \ ]$ describes one electron occupying a $2s-a2p_x$ polarized orbital while the other electron occupies the $2s+a2p_x$ orbital. In this picture, the electrons reduce their mutual coulomb repulsion by occupying different regions of space; in the SCF mean-field picture, both electrons reside in the same 2s region of space. In this particular example, the electrons undergo angular correlation to "avoid" one another. The fact that equal amounts of x, y, and z orbital polarization appear in   is what preserves the ^1S symmetry of the wavefunction.

The fact that the CI wavefunction

$$C_1 |1s^22s^2| - C_2 [|1s^22p_x^2| + |1s^22p_y^2| + |1s^22p_z^2|]$$

mixes its two configurations with <u>opposite sign</u> is of significance. As will be seen later in Section 6, solution of the Schrödinger equation using the CI method in which two configurations (e.g., $|1s^22s^2|$ and $|1s^22p^2|$) are employed gives rise to two solutions. One approximates the ground state wave function; the other approximates an excited state. The former is the one that mixes the two configurations with opposite sign.

To understand why the latter is of higher energy, it suffices to analyze a function of the form

$$\Psi' \quad C_1 |1s^22s^2| + C_2 [|1s^22p_x^2| + |1s^22p_y^2| + |1s^22p_z^2|]$$

in a manner analogous to above. In this case, it can be shown that

$$\Psi' \quad 1/6 \, C_1 |1s^2\{[(2s-ia2p_x)(2s+ia2p_x) - (2s-ia2p_x)(2s+ia2p_x)]$$

$$+[(2s-ia2p_y)(2s+ia2p_y) - (2s-ia2p_y)(2s+ia2p_y)]$$

$$+[(2s-ia2p_z)(2s+ia2p_z) - (2s-ia2p_z)(2s+ia2p_z)]|\}.$$

There is a fundamental difference, however, between the polarized orbital pairs introduced earlier $\phi_\pm = (2s \pm a2p_{x,y,or\ z})$ and the corresponding functions $\phi'_\pm = (2s \pm ia2p_{x,y,or\ z})$ appearing here. The probability densities embodied in the former

$$|\phi_\pm|^2 = |2s|^2 + a^2 |2p_{x,y,or\ z}|^2 \pm 2a(2s\ 2p_{x,y,or\ z})$$

describe constructive (for the + case) and destructive (for the - case) superposition of the probabilities of the 2s and 2p orbitals. The probability densities of $\phi'_\pm$ are

$$|\phi'_\pm|^2 = (2s \pm ia2p_{x,y,or\ z})^*(2s \pm ia2p_{x,y,or\ z})$$

$$= |2s|^2 + a^2 |2p_{x,y,or\ z}|^2 .$$

These densities are identical to one another and do not describe polarized orbital densities. Therefore, the CI wavefunction which mixes the two configurations with like sign, when analyzed in terms of orbital pairs, places the electrons into orbitals $'_\pm = (2s \pm ia2p_{x,y,or\ z})$ whose densities do not permit the electrons to avoid one another. Rather, both orbitals have the same spatial density $|2s|^2 + a^2$ $|2p_{x,y,or\ z}|^2$, which gives rise to higher coulombic interaction energy for this state.

V. Summary

In summary, the dynamical interactions among electrons give rise to instantaneous spatial correlations that must be handled to arrive at an accurate picture of atomic and molecular structure. The simple, single-configuration picture provided by the mean-field model is a useful starting point, but improvements are often needed.
In Section 6, methods for treating electron correlation will be discussed in greater detail.

For the remainder of this Section, the primary focus is placed on forming proper N-electron wavefunctions by occupying the orbitals available to the system in a manner that guarantees that the resultant N-electron function is an eigenfunction of those operators that commute with the N-electron Hamiltonian.

For polyatomic molecules, these operators include point-group symmetry operators (which act on all N electrons) and the spin angular momentum (S^2 and S_z) of all of the electrons taken as a whole (this is true in the absence of spin-orbit coupling which is treated later as a perturbation). For linear molecules, the point group symmetry operations involve rotations R_z of all N electrons about the principal axis, as a result of which the total angular momentum L_z of the N electrons (taken as a whole) about this axis commutes with the Hamiltonian, H. Rotation of all N electrons about the x and y axes does not leave the total coulombic potential energy unchanged, so L_x and L_y do not commute with H. Hence for a linear molecule, L_z, S^2, and S_z are the operators that commute with H. For atoms, the corresponding operators are L^2, L_z, S^2, and S_z (again, in the absence of spin-orbit coupling) where each operator pertains to the total orbital or spin angular momentum of the N electrons.

To construct N-electron functions that are eigenfunctions of the spatial symmetry or orbital angular momentum operators as well as the spin angular momentum operators, one has to "couple" the symmetry or angular momentum properties of the individual spin-orbitals used to construct the N-electrons functions. This coupling involves forming direct product symmetries in the case of polyatomic molecules that belong to finite point groups,

it involves vector coupling orbital and spin angular momenta in the case of atoms, and it involves vector coupling spin angular momenta and axis coupling orbital angular momenta when treating linear molecules. Much of this Section is devoted to developing the tools needed to carry out these couplings.

Chapter 9

Electronic Wavefuntions Must be Constructed to Have Permutational Antisymmetry Because the N Electrons are Indistinguishable Fermions

I. Electronic Configurations

Atoms, linear molecules, and non-linear molecules have orbitals which can be labeled either according to the symmetry appropriate for that isolated species or for the species in an environment which produces lower symmetry. These orbitals should be viewed as regions of space in which electrons can move, with, of course, at most two electrons (of opposite spin) in each orbital. Specification of a particular occupancy of the set of orbitals available to the system gives an <u>electronic configuration</u>. For example, $1s^22s^22p^4$ is an electronic configuration for the Oxygen atom (and for the F^{+1} ion and the N^{-1} ion); $1s^22s^22p^33p^1$ is another configuration for O, F^{+1}, or N^{-1}. These configurations represent situations in which the electrons occupy low-energy orbitals of the system and, as such, are likely to contribute strongly to the true ground and low-lying excited states and to the low-energy states of molecules formed from these atoms or ions.

Specification of an electronic configuration does not, however, specify a particular electronic state of the system. In the above $1s^22s^22p^4$ example, there are many ways (fifteen, to be precise) in which the 2p orbitals can be occupied by the four electrons. As a result, there are a total of fifteen states which cluster into three energetically distinct <u>levels</u>, lying within this single configuration. The $1s^22s^22p^33p^1$ configuration contains thirty-six states which group into six distinct energy levels (the word <u>level</u> is used to denote one or more state with the same energy). Not all states which arise from a given electronic configuration have the same energy because various states occupy the degenerate (e.g., 2p and 3p in the above examples) orbitals differently. That is, some states have orbital

occupancies of the form $2p^2_1 2p^1_0 2p^1_{-1}$ while others have $2p^2_1 2p^2_0 2p^0_{-1}$; as a result, the states can have quite different coulombic repulsions among the electrons (the state with two doubly occupied orbitals would lie higher in energy than that with two singly occupied orbitals). Later in this Section and in Appendix G techniques for constructing wavefunctions for each state contained within a particular configuration are given in detail. Mastering these tools is an important aspect of learning the material in this text.

In summary, an atom or molecule has many orbitals (core, bonding, non-bonding, Rydberg, and antibonding) available to it; occupancy of these orbitals in a particular manner gives rise to a configuration. If some orbitals are partially occupied in this configuration, more than one state will arise; these states can differ in energy due to differences in how the orbitals are occupied. In particular, if degenerate orbitals are partially occupied, many states can arise and have energies which differ substantially because of differences in electron repulsions arising in these states. Systematic procedures for extracting all states from a given configuration, for labeling the states according to the appropriate symmetry group, for writing the wavefunctions corresponding to each state and for evaluating the energies corresponding to these wavefunctions are needed. Much of Chapters 10 and 11 are devoted to developing and illustrating these tools.

II. Antisymmetric Wavefunctions

A. General Concepts

The total electronic Hamiltonian

$$H = \sum_i (-\hbar^2/2m_e \nabla_i^2 - \sum_a Z_a e^2/r_{ia}) + \sum_{i>j} e^2/r_{ij} + \sum_{a>b} Z_a Z_b e^2/r_{ab},$$

where i and j label electrons and a and b label the nuclei (whose charges are denoted Z_a), commutes with the operators P_{ij} which permute the names of the electrons i and j. This, in turn, requires eigenfunctions of H to be eigenfunctions of P_{ij}. In fact, the set of such permutation operators form a group called the symmetric group (a good reference to this subject is contained in Chapter 7 of Group Theory , M. Hamermesh, Addison-Wesley, Reading, Mass. (1962)). In the present text, we will not exploit the full group theoretical nature of these operators; we will focus on the simple fact that all wavefunctions must be eigenfunctions of the P_{ij} (additional material on this subject is contained in Chapter XIV of Kemble).

Because P_{ij} obeys $P_{ij} * P_{ij} = 1$, the eigenvalues of the P_{ij} operators must be +1 or -1. Electrons are Fermions (i.e., they have half-integral spin), and they have wavefunctions which are odd under permutation of any pair: $P_{ij} \Psi = -\Psi$. Bosons such as photons or deuterium nuclei (i.e., species with integral spin quantum numbers) have wavefunctions which obey $P_{ij} \Psi = +\Psi$.

These permutational symmetries are not only characteristics of the exact eigenfunctions of H belonging to any atom or molecule containing more than a single electron but they are also conditions which must be placed on any acceptable model or trial wavefunction (e.g., in a variational sense) which one constructs.

In particular, within the orbital model of electronic structure (which is developed more systematically in Section 6), one can not construct trial wavefunctions which are simple spin-orbital products (i.e., an orbital multiplied by an α or β spin function for each electron) such as $1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_1\alpha\ 2p_0\alpha$. Such spin-orbital product functions <u>must</u> be made permutationally antisymmetric if the N-electron trial function is to be properly antisymmetric. This can be accomplished for any such product wavefunction by applying the following <u>antisymmetrizer operator</u>:

$$A = (\sqrt{1/N!}) \sum_p s_p\ P,$$

where N is the number of electrons, P runs over all N! permutations, and s_p is +1 or -1 depending on whether the permutation P contains an even or odd number of pairwise permutations (e.g., 231 can be reached from 123 by two pairwise permutations-123==>213==>231, so 231 would have s_p =1). The permutation operator P in A acts on a product wavefunction and permutes the ordering of the spin-orbitals. For example, A $\phi_1\ \phi_2\ \phi_3 = (1/\sqrt{6}) [\phi_1\ \phi_2\ \phi_3 - \phi_1\ \phi_3\ \phi_2 - \phi_3\ \phi_2\ \phi_1 - \phi_2\ \phi_1\ \phi_3 + \phi_3\ \phi_1\ \phi_2 + \phi_2\ \phi_3\ \phi_1]$, where the convention is that electronic coordinates r_1, r_2, and r_3 correspond to the orbitals as they appear in the product (e.g., the term $\phi_3\ \phi_2\ \phi_1$ represents $\phi_3(r_1)\ \phi_2(r_2)\ \phi_1(r_3)$).

It turns out that the permutations P can be allowed either to act on the "names" or labels of the electrons, keeping the order of the spin-orbitals fixed, or to act on the spin-orbitals, keeping the order and identity of the electrons' labels fixed. The resultant wavefunction, which contains N! terms, is exactly the same regardless of how one allows the permutations to act. Because we wish to use the above convention in which the order of the electronic labels remains fixed as 1, 2, 3, ... N, we choose to think of the permutations acting on the names of the spin-orbitals.

It should be noted that the effect of A on any spin-orbital product is to produce a function that is a sum of N! terms. In each of these terms the same spin-orbitals appear, but

the order in which they appear differs from term to term. Thus antisymmetrization does not alter the overall orbital occupancy; it simply "scrambles" any knowledge of which electron is in which spin-orbital.

The antisymmetrized orbital product $A\ \phi_1\phi_2\phi_3$ is represented by the short hand $|\phi_1\phi_2\phi_3|$ and is referred to as a <u>Slater determinant</u>. The origin of this notation can be made clear by noting that $(1/\sqrt{N!})$ times the determinant of a matrix whose rows are labeled by the index i of the spin-orbital ϕ_i and whose columns are labeled by the index j of the electron at $\mathbf{r}_j$ is equal to the above function: $A\ \phi_1\phi_2\phi_3 = (1/\sqrt{3!})\ \det(\phi_i(\mathbf{r}_j))$. The general structure of such Slater determinants is illustrated below:

$$(1/N!)^{1/2}\ \det\{\phi_j(\mathbf{r}_i)\} = (1/N!)^{1/2}\begin{bmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1)... & \phi_k(1)....... & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \phi_3(2)... & \phi_k(2)....... & \phi_N(2) \\ . \\ . \\ . \\ . \\ \phi_1(\ ) & \phi_2(\ ) & \phi_3(\ ).. & \phi_k(\ ).. & \phi_N(\ ) \end{bmatrix}$$

The antisymmetry of many-electron spin-orbital products places constraints on any acceptable model wavefunction, which give rise to important physical consequences. For example, it is antisymmetry that makes a function of the form $|1s\alpha\ 1s\alpha|$ vanish (thereby enforcing the Pauli exclusion principle) while $|1s\alpha\ 2s\alpha|$ does not vanish, except at points $\mathbf{r}_1$ and $\mathbf{r}_2$ where $1s(\mathbf{r}_1) = 2s(\mathbf{r}_2)$, and hence is acceptable. The Pauli principle is embodied in the fact that if any two or more columns (or rows) of a determinant are identical, the determinant vanishes. Antisymmetry also enforces indistinguishability of the electrons in that $|1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta| =$
$-|1s\alpha\ 1s\beta\ 2s\beta\ 2s\alpha|$. That is, two wavefunctions which differ simply by the ordering of their spin-orbitals are equal to within a sign (+/- 1); such an overall sign difference in a wavefunction has no physical consequence because all physical properties depend on the product $\psi^* \psi$, which appears in any expectation value expression.

B. Physical Consequences of Antisymmetry

Once the rules for evaluating energies of determinental wavefunctions and for forming functions which have proper spin and spatial symmetries have been put forth (in Chapter 11), it will be clear that antisymmetry and electron spin considerations, in addition to orbital occupancies, play substantial roles in determining energies and that it is precisely

these aspects that are responsible for energy splittings among states arising from one configuration. A single example may help illustrate this point. Consider the $\pi^1 \pi^{*1}$ configuration of ethylene (ignore the other orbitals and focus on the properties of these two). As will be shown below when spin angular momentum is treated in full, the triplet spin states of this configuration are:

$$|S=1, M_S=1> = |\pi \pi^* |,$$

$$|S=1, M_S=-1> = |\bar{\pi} \bar{\pi}^* |,$$

and

$$|S=1, M_S= 0> = 2^{-1/2}[|\pi \bar{\pi}^* | + |\bar{\pi} \pi^* |].$$

The singlet spin state is:

$$|S=0, M_S= 0> = 2^{-1/2}[|\pi \bar{\pi}^* | - |\bar{\pi} \pi^* |].$$

To understand how the three triplet states have the same energy and why the singlet state has a different energy, and an energy different than the $M_S= 0$ triplet even though these two states are composed of the same two determinants, we proceed as follows:

1. We express the bonding π and antibonding π^* orbitals in terms of the atomic p-orbitals from which they are formed: $\pi = 2^{-1/2} [L + R]$ and $\pi^* = 2^{-1/2} [L - R]$, where R and L denote the p-orbitals on the left and right carbon atoms, respectively.

2. We substitute these expressions into the Slater determinants that form the singlet and triplet states and collect terms and throw out terms for which the determinants vanish.

3. This then gives the singlet and triplet states in terms of atomic-orbital occupancies where it is easier to see the energy equivalences and differences.

Let us begin with the triplet states:

$$|\pi \pi^* | = 1/2 [|L \bar{L} | - |R \bar{R} | + |R \bar{L} | - |L \bar{R} |]$$

$$= |R \bar{L} |;$$

$$2^{-1/2}[|\quad * \quad| + |\quad * \quad|] = 2^{-1/2}\ 1/2[\ |L\ \ L\ | - |R\ \ R\ | + |R\ \ L\ | -$$

$$|L\ \ R\ | + |L\ \ L\ | - |R\ \ R\ | + |R\ \ L\ | - |L\ \ R\ |\ ]$$

$$= 2^{-1/2}\ [\ |R\ \ L\ | + |R\ \ L\ |\ ];$$

$$|\quad * \quad| = 1/2\ [\ |L\ \ L\ | - |R\ \ R\ | + |R\ \ L\ | - |L\ \ R\ |\ ]$$

$$= |R\ \ L\ |.$$

The singlet state can be reduced in like fashion:

$$2^{-1/2}[|\quad * \quad| - |\quad * \quad|] = 2^{-1/2}\ 1/2[\ |L\ \ L\ | - |R\ \ R\ | + |R\ \ L\ | -$$

$$|L\ \ R\ | - |L\ \ L\ | + |R\ \ R\ | - |R\ \ L\ | + |L\ \ R\ |\ ]$$

$$= 2^{-1/2}\ [\ |L\ \ L\ | - |R\ \ R\ |\ ].$$

Notice that all three triplet states involve atomic orbital occupancy in which one electron is on one atom while the other is on the second carbon atom. In contrast, the singlet state places both electrons on one carbon (it contains two terms; one with the two electrons on the left carbon and the other with both electrons on the right carbon).

In a "valence bond" analysis of the physical content of the singlet and triplet [1] [*1] states, it is clear that the energy of the triplet states will lie below that of the singlet because the singlet contains "zwitterion" components that can be denoted C^+C^- and C^-C^+, while the three triplet states are purely "covalent". This case provides an excellent example of how the spin and permutational symmetries of a state "conspire" to qualitatively affect its energy and even electronic character as represented in its atomic orbital occupancies. Understanding this should provide ample motivation for learning how to form proper antisymmetric spin (and orbital) angular momentum eigenfunctions for atoms and molecules.

Chapter 10

Electronic Wavefunctions Must Also Possess Proper Symmetry. These Include Angular Momentum and Point Group Symmetries

I. Angular Momentum Symmetry and Strategies for Angular Momentum Coupling

Because the total Hamiltonian of a many-electron atom or molecule forms a mutually commutative set of operators with S^2, S_z, and $A = (1/N!) \sum_p s_p P$, the exact eigenfunctions of H must be eigenfunctions of these operators. Being an eigenfunction of *A* forces the eigenstates to be odd under all P_{ij}. Any acceptable model or trial wavefunction should be constrained to also be an eigenfunction of these symmetry operators.

If the atom or molecule has additional symmetries (e.g., full rotation symmetry for atoms, axial rotation symmetry for linear molecules and point group symmetry for non-linear polyatomics), the trial wavefunctions should also conform to these spatial symmetries. This Chapter addresses those operators that commute with H, P_{ij}, S^2, and S_z and among one another for atoms, linear, and non-linear molecules.

As treated in detail in Appendix G, the full non-relativistic N-electron Hamiltonian of an atom or molecule

$$H = \sum_j (- \hbar^2/2m \nabla_j^2 - \sum_a Z_a e^2/r_{j,a}) + \sum_{j<k} e^2/r_{j,k}$$

commutes with the following operators:

i. The inversion operator i and the three components of the total orbital angular momentum $L_z = \sum_j L_z(j)$, L_y, L_x, as well as the components of the total spin angular momentum S_z, S_x, and S_y **for atoms** (but not the individual electrons' $L_z(j)$, $S_z(j)$, etc). Hence, L^2, L_z, S^2, S_z are the operators we need to form eigenfunctions of, and L, M_L, S, and M_S are the "good" quantum numbers.

ii. $L_z = \sum_j L_z(j)$, as well as the N-electron S_x, S_y, and S_z **for linear molecules** (also i, if the molecule has a center of symmetry). Hence, L_z, S^2, and S_z are the operators we need to

form eigenfunctions of, and M_L, S, and M_S are the "good" quantum numbers; L no longer is!

iii. S_x, S_y, and S_z as well as all point group operations **for non-linear polyatomic molecules**. Hence S^2, S_z, and the point group operations are used to characterize the functions we need to form. When we include spin-orbit coupling into H (this adds another term to the potential that involves the spin and orbital angular momenta of the electrons), L^2, L_z, S^2, S_z no longer commute with H. However, $J_z = S_z + L_z$ and $J^2 = (\mathbf{L+S})^2$ now do commute with H.

A. Electron Spin Angular Momentum

Individual electrons possess intrinsic spin characterized by angular momentum quantum numbers s and m_s ; for electrons, s = 1/2 and m_s = 1/2, or -1/2. The m_s =1/2 spin state of the electron is represented by the symbol   and the m_s = -1/2 state is represented by
  . These spin functions obey: S^2 = 1/2 (1/2 + 1)$\hbar^2$,
S_z = 1/2$\hbar$, S^2 =1/2 (1/2 + 1) $\hbar^2$, and S_z = -1/2$\hbar$. The   and   spin functions are connected via lowering S_- and raising S_+ operators, which are defined in terms of the x and y components of **S** as follows: $S_+ = S_x + iS_y$, and $S_- = S_x - iS_y$. In particular S_+ =
$\hbar$, S_+ =0, S_- = $\hbar$,
and S_- =0. These expressions are examples of the more general relations (these relations are developed in detail in Appendix G) which all angular momentum operators and their eigenstates obey:

J^2 |j,m> = j(j+1)$\hbar^2$ |j,m>,

J_z |j,m> = m$\hbar$ |j,m>,

J_+ |j,m> =$\hbar$ {j(j+1)-m(m+1)}$^{1/2}$ |j,m+1>, and

J_- |j,m> =$\hbar$ {j(j+1)-m(m-1)}$^{1/2}$ |j,m-1>.

In a many-electron system, one must combine the spin functions of the individual electrons to generate eigenfunctions of the total $S_z = \sum_i S_z(i)$ (expressions for $S_x = \sum_i S_x(i)$ and $S_y = \sum_i S_y(i)$ also follow from the fact that the total angular momentum of a collection of particles is the sum of the angular momenta, component-by-component, of the individual

angular momenta) and total S^2 operators because only these operators commute with the full Hamiltonian, H, and with the permutation operators P_{ij}. No longer are the individual $S^2(i)$ and $S_z(i)$ good quantum numbers; these operators do not commute with P_{ij}.

Spin states which are eigenfunctions of the total S^2 and S_z can be formed by using angular momentum coupling methods or the explicit construction methods detailed in Appendix (G). In the latter approach, one forms, consistent with the given electronic configuration, the spin state having maximum S_z eigenvalue (which is easy to identify as shown below and which corresponds to a state with S equal to this maximum S_z eigenvalue) and then generating states of lower S_z values and lower S values using the angular momentum raising and lowering operators ($S_- = \sum_i S_-(i)$ and $S_+ = \sum_i S_+(i)$).

To illustrate, consider a three-electron example with the configuration 1s2s3s. Starting with the determinant $| 1s\alpha\ 2s\alpha\ 3s\alpha\ |$, which has the maximum M_s =3/2 and hence has S=3/2 (this function is denoted |3/2, 3/2>), apply S_- in the additive form $S_- = \sum_i S_-(i)$ to generate the following combination of three determinants:

$$\hbar[| 1s\beta\ 2s\alpha\ 3s\alpha\ | + | 1s\alpha\ 2s\beta\ 3s\alpha\ | + | 1s\alpha\ 2s\alpha\ 3s\beta\ |],$$

which, according to the above identities, must equal

$$\hbar\sqrt{3/2(3/2+1)-3/2(3/2-1)}\ | 3/2,\ 1/2>.$$

So the state |3/2, 1/2> with S=3/2 and M_s =1/2 can be solved for in terms of the three determinants to give

|3/2, 1/2> = 1/$\sqrt{3}$ [| 1sβ 2sα 3sα | + | 1sα 2sβ 3sα | + | 1sα 2sα 3sβ |].
The states with S=3/2 and M_s = -1/2 and -3/2 can be obtained by further application of S_- to |3/2, 1/2> (actually, the M_s= -3/2 can be identified as the "spin flipped" image of the state with M_s =3/2 and the one with M_s =-1/2 can be formed by interchanging all α's and β's in the M_s = 1/2 state).

Of the eight total spin states (each electron can take on either α or β spin and there are three electrons, so the number of states is 2^3), the above process has identified proper combinations which yield the four states with S= 3/2. Doing so consumed the determinants with M_s =3/2 and -3/2, one combination of the three determinants with M_S =1/2, and one combination of the three determinants with M_s =-1/2. There still remain two combinations

of the $M_s = 1/2$ and two combinations of the $M_s = -1/2$ determinants to deal with. These functions correspond to two sets of $S = 1/2$ eigenfunctions having $M_s = 1/2$ and $-1/2$. Combinations of the determinants must be used in forming the $S = 1/2$ functions to keep the $S = 1/2$ eigenfunctions orthogonal to the above $S = 3/2$ functions (which is required because S^2 is a hermitian operator whose eigenfunctions belonging to different eigenvalues must be orthogonal). The two independent $S = 1/2$, $M_s = 1/2$ states can be formed by simply constructing combinations of the above three determinants with $M_s = 1/2$ which are orthogonal to the $S = 3/2$ combination given above and orthogonal to each other. For example,

$| 1/2, 1/2> = 1/\ 2[| 1s\ \ 2s\ \ 3s\ \ | - | 1s\ \ 2s\ \ 3s\ \ | + 0x | 1s\ \ 2s\ \ 3s\ \ |],$

$| 1/2, 1/2> = 1/\ 6[| 1s\ \ 2s\ \ 3s\ \ | + | 1s\ \ 2s\ \ 3s\ \ | -2x | 1s\ \ 2s\ \ 3s\ \ |]$

are acceptable (as is any combination of these two functions generated by a unitary transformation). A pair of independent orthonormal states with $S = 1/2$ and $M_s = -1/2$ can be generated by applying S_- to each of these two functions (or by constructing a pair of orthonormal functions which are combinations of the three determinants with $M_s = -1/2$ and which are orthogonal to the $S = 3/2$, $M_s = -1/2$ function obtained as detailed above).

The above treatment of a three-electron case shows how to generate quartet (spin states are named in terms of their spin degeneracies $2S+1$) and doublet states for a configuration of the form 1s2s3s. Not all three-electron configurations have both quartet and doublet states; for example, the $1s^2\ 2s$ configuration only supports one doublet state. The methods used above to generate $S = 3/2$ and $S = 1/2$ states are valid for any three-electron situation; however, some of the determinental functions vanish if doubly occupied orbitals occur as for $1s^2 2s$. In particular, the $| 1s\ \ 1s\ \ 2s\ \ |$ and $| 1s\ \ 1s\ \ 2s\ \ |$ $M_s = 3/2, -3/2$ and $| 1s\ \ 1s\ \ 2s\ \ |$ and $| 1s\ \ 1s\ \ 2s\ \ |$ $M_s = 1/2, -1/2$ determinants vanish because they violate the Pauli principle; only $| 1s\ \ 1s\ \ 2s\ \ |$ and $| 1s\ \ 1s\ \ 2s\ \ |$ do not vanish. These two remaining determinants form the $S = 1/2$, $M_s = 1/2$, $-1/2$ doublet spin functions which pertain to the $1s^2 2s$ configuration. It should be noted that all closed-shell components of a configuration (e.g., the $1s^2$ part of $1s^2 2s$ or the $1s^2 2s^2\ 2p^6$ part of $1s^2 2s^2\ 2p^6 3s^1 3p^1$) must involve   and   spin functions for each doubly occupied orbital and, as such, can contribute nothing to the total M_s value; only the open-shell

components need to be treated with the angular momentum operator tools to arrive at proper total-spin eigenstates.

In summary, proper spin eigenfunctions must be constructed from antisymmetric (i.e., determinental) wavefunctions as demonstrated above because the total S^2 and total S_z remain valid symmetry operators for many-electron systems. Doing so results in the spin-adapted wavefunctions being expressed as combinations of determinants with coefficients determined via spin angular momentum techniques as demonstrated above. In configurations with closed-shell components, not all spin functions are possible because of the antisymmetry of the wavefunction; in particular, any closed-shell parts must involve spin pairings for each of the doubly occupied orbitals, and, as such, contribute zero to the total M_s.

B. Vector Coupling of Angular Momenta

Given two angular momenta (of any kind) $\mathbf{L}_1$ and $\mathbf{L}_2$, when one generates states that are eigenstates of their vector sum $\mathbf{L}= \mathbf{L}_1+\mathbf{L}_2$,
one can obtain L values of L_1+L_2, L_1+L_2-1, ...$|L_1-L_2|$. This can apply to two electrons for which the total spin S can be 1 or 0 as illustrated in detail above, or to a p and a d orbital for which the total orbital angular momentum L can be 3, 2, or 1. Thus for a p^1d^1 electronic configuration, ^3F, ^1F, ^3D, ^1D, ^3P, and ^1P energy levels (and corresponding wavefunctions) arise. Here the term symbols are specified as the spin degeneracy (2S+1) and the letter that is associated with the L-value. If spin-orbit coupling is present, the ^3F level further splits into J= 4, 3, and 2 levels which are denoted $^3F_4$, $^3F_3$, and $^3F_2$.

This simple "vector coupling" method applies to any angular momenta. However, if the angular momenta are "equivalent" in the sense that they involve indistinguishable particles that occupy the same orbital shell (e.g., $2p^3$ involves 3 equivalent electrons; $2p^13p^14p^1$ involves 3 non-equivalent electrons; $2p^23p^1$ involves 2 equivalent electrons and one non-equivalent electron), the Pauli principle eliminates some of the expected term symbols (i.e., when the corresponding wavefunctions are formed, some vanish because their Slater determinants vanish). Later in this section, techniques for dealing with the equivalent-angular momenta case are introduced. These techniques involve using the above tools to obtain a list of candidate term symbols after which Pauli-violating term symbols are eliminated.

C. Non-Vector Coupling of Angular Momenta

For linear molecules, one does <u>not</u> vector couple the orbital angular momenta of the individual electrons (because only L_z not L^2 commutes with H), but one does vector couple the electrons' spin angular momenta. Coupling of the electrons' orbital angular momenta involves simply considering the various L_z eigenvalues that can arise from adding the L_z values of the individual electrons. For example, coupling two π orbitals (each of which can have m = ±1) can give M_L=1+1, 1-1, -1+1, and -1-1, or 2, 0, 0, and -2. The level with $M_L = \pm 2$ is called a Δ state (much like an orbital with m = ±2 is called a δ orbital), and the two states with $M_L = 0$ are called Σ states. States with L_z eigenvalues of M_L and - M_L are degenerate because the total energy is independent of which direction the electrons are moving about the linear molecule's axis (just a π$_{+1}$ and π$_{-1}$ orbitals are degenerate).

Again, if the two electrons are non-equivalent, all possible couplings arise (e.g., a π^1 π'^{1} configuration yields $^3\Sigma$, $^3\Sigma$, $^3\Delta$, $^1\Sigma$, $^1\Sigma$, and $^1\Delta$ states). In contrast, if the two electrons are equivalent, certain of the term symbols are Pauli forbidden. Again, techniques for dealing with such cases are treated later in this Chapter.

D. Direct Products for Non-Linear Molecules

For non-linear polyatomic molecules, one vector couples the electrons' spin angular momenta but their orbital angular momenta are not even considered. Instead, their point group symmetries must be combined, by forming direct products, to determine the symmetries of the resultant spin-orbital product states. For example, the $b_1^1 b_2^1$ configuration in C_{2v} symmetry gives rise to $^3A_2$ and $^1A_2$ term symbols. The $e^1 e'^1$ configuration in C_{3v} symmetry gives ^3E, $^3A_2$, $^3A_1$, ^1E, $^1A_2$, and $^1A_1$ term symbols. For two equivalent electrons such as in the e^2 configuration, certain of the ^3E, $^3A_2$, $^3A_1$, ^1E, $^1A_2$, and $^1A_1$ term symbols are Pauli forbidden. Once again, the methods needed to identify which term symbols arise in the equivalent-electron case are treated later.

One needs to learn how to tell which term symbols will be Pauli excluded, and to learn how to write the spin-orbit product wavefunctions corresponding to each term symbol and to evaluate the corresponding term symbols' energies.

II. Atomic Term Symbols and Wavefunctions

A. Non-Equivalent Orbital Term Symbols

When coupling non-equivalent angular momenta (e.g., a spin and an orbital angular momenta or two orbital angular momenta of non-equivalent electrons), one vector couples

using the fact that the coupled angular momenta range from the sum of the two individual angular momenta to the absolute value of their difference. For example, when coupling the spins of two electrons, the total spin S can be 1 or 0; when coupling a p and a d orbital, the total orbital angular momentum can be 3, 2, or 1. Thus for a p^1d^1 electronic configuration, ^3F, ^1F, ^3D, ^1D, ^3P, and ^1P energy levels (and corresponding wavefunctions) arise. The energy differences among these levels has to do with the different electron-electron repulsions that occur in these levels; that is, their wavefunctions involve different occupancy of the p and d orbitals and hence different repulsion energies. If spin-orbit coupling is present, the L and S angular momenta are further vector coupled. For example, the ^3F level splits into J= 4, 3, and 2 levels which are denoted $^3F_4$, $^3F_3$, and $^3F_2$. The energy differences among these J-levels are caused by spin-orbit interactions.

B. Equivalent Orbital Term Symbols

If equivalent angular momenta are coupled (e.g., to couple the orbital angular momenta of a p^2 or d^3 configuration), one must use the "box" method to determine which of the term symbols, that would be expected to arise if the angular momenta were non-equivalent, violate the Pauli principle. To carry out this step, one forms all possible unique (determinental) product states with non-negative M_L and M_S values and arranges them into groups according to their M_L and M_S values. For example, the boxes appropriate to the p^2 orbital occupancy are shown below:

M_L	2	1	0
M_S 1		$|p_1\ p_0\ |$	$|p_1\ p_{-1}\ |$
0	$|p_1\ p_1\ |$	$|p_1\ p_0\ |, |p_0\ p_1\ |$	$|p_1\ p_{-1}\ |,$ $|p_{-1}\ p_1\ |,$ $|p_0\ p_0\ |$

There is no need to form the corresponding states with negative M_L or negative M_S values because they are simply "mirror images" of those listed above. For example, the state with $M_L = -1$ and $M_S = -1$ is $|p_{-1}\ p_0\ |$, which can be obtained from the $M_L = 1$, $M_S = 1$ state $|p_1\ p_0\ |$ by replacing by and replacing p_1 by p_{-1}.

Given the box entries, one can identify those term symbols that arise by applying the following procedure over and over until all entries have been accounted for:

1. One identifies the highest M_S value (this gives a value of the total spin quantum number that arises, S) in the box. For the above example, the answer is S = 1.
2. For all product states of <u>this</u> M_S value, one identifies the highest M_L value (this gives a value of the total orbital angular momentum, L, that can arise <u>for this S</u>). For the above example, the highest M_L within the $M_S =1$ states is $M_L = 1$ (not $M_L = 2$), hence L=1.
3. Knowing an S, L combination, one knows the first term symbol that arises from this configuration. In the p^2 example, this is ^3P.
4. Because the level with this L and S quantum numbers contains (2L+1)(2S+1) states with M_L and M_S quantum numbers running from -L to L and from -S to S, respectively, one must remove from the original box this number of product states. To do so, one simply erases from the box one entry with each such M_L and M_S value. Actually, since the box need only show those entries with non-negative M_L and M_S values, only these entries need be explicitly deleted. In the ^3P example, this amounts to deleting nine product states with M_L, M_S values of 1,1; 1,0; 1,-1; 0,1; 0,0; 0,-1; -1,1; -1,0; -1,-1.
5. After deleting these entries, one returns to step 1 and carries out the process again. For the p^2 example, the box after deleting the first nine product states looks as follows (those that appear in italics should be viewed as already cancelled in counting all of the ^3P states):

M_L	2	1	0

M_S			
1		*|p₁ p₀ |*	*|p₁ p₋₁ |*
0	|p₁ p₁		*|p₁ p₀ |,* |p₀ p₁		*|p₁ p₋₁ |,* |p₋₁ p₁ |, |p₀ p₀	

It should be emphasized that the process of deleting or crossing off entries in various M_L, M_S boxes involves only <u>counting</u> how many states there are; by no means do we identify the particular L,S,M_L,M_S wavefunctions when we cross out any particular entry in a box. For example, when the |p₁ p₀ | product is deleted from the $M_L= 1$, $M_S=0$ box in accounting for the states in the ^3P level, we do not claim that |p₁ p₀ | itself is a member of the ^3P level; the |p₀ p₁ | product state could just as well been eliminated when accounting for the ^3P states. As will be shown later, the ^3P state with $M_L= 1$, $M_S=0$ will be a combination of |p₁ p₀ | and |p₀ p₁ |.

Returning to the p^2 example at hand, after the ^3P term symbol's states have been accounted for, the highest M_S value is 0 (hence there is an S=0 state), and within this M_S value, the highest M_L value is 2 (hence there is an L=2 state). This means there is a ^1D level with five states having $M_L = 2,1,0,-1,-2$. Deleting five appropriate entries from the above box (again denoting deletions by italics) leaves the following box:

M_L	2	1	0
M_S 1		$|p_1 \; p_0|$	$|p_1 \; p_{-1}|$
0	$|p_1 \; p_1|$	$|p_1 \; p_0|, |p_0 \; p_1|$	$|p_1 \; p_{-1}|,$ $|p_{-1} \; p_1|,$ $|p_0 \; p_0|$

The only remaining entry, which thus has the highest M_S and M_L values, has $M_S = 0$ and $M_L = 0$. Thus there is also a ^1S level in the p^2 configuration.

Thus, unlike the non-equivalent $2p^13p^1$ case, in which ^3P, ^1P, ^3D, ^1D, ^3S, and ^1S levels arise, only the ^3P, ^1D, and ^1S arise in the p^2 situation. This "box method" is necessary to carry out whenever one is dealing with equivalent angular momenta.

If one has mixed equivalent and non-equivalent angular momenta, one can determine <u>all</u> possible couplings of the equivalent angular momenta using this method and then use the simpler vector coupling method to add the non-equivalent angular momenta to <u>each</u> of these coupled angular momenta. For example, the p^2d^1 configuration can be handled by vector coupling (using the straightforward non-equivalent procedure) L=2 (the d orbital) and S=1/2 (the third electron's spin) to <u>each</u> of ^3P, ^1D, and ^1S. The result is ^4F, ^4D, ^4P, ^2F, ^2D, ^2P, ^2G, ^2F, ^2D, ^2P, ^2S, and ^2D.

C. Atomic Configuration Wavefunctions

To express, in terms of Slater determinants, the wavefunctions corresponding to each of the states in each of the levels, one proceeds as follows:

1. For each M_S, M_L combination for which one can write down only one product function (i.e., in the non-equivalent angular momentum situation, for each case where only one product function sits at a given box row and column point), that product function <u>itself</u> is one of the desired states. For the p^2 example, the $|p_1 \; p_0|$ and $|p_1 \; p_{-1}|$ (as well as their four other M_L and M_S "mirror images") are members of the ^3P level (since they have $M_S = \pm1$) and $|p_1 \; p_1|$ and its M_L mirror image are members of the ^1D level (since they have $M_L = \pm2$).

2. After identifying as many such states as possible by inspection, one uses $L_\pm$ and $S_\pm$ to generate states that belong to the same term symbols as those already identified but which have higher or lower M_L and/or M_S values.

3. If, after applying the above process, there are term symbols for which states have not yet been formed, one may have to construct such states by forming linear combinations that are orthogonal to all those states that have thus far been found.

To illustrate the use of raising and lowering operators to find the states that can not be identified by inspection, let us again focus on the p^2 case. Beginning with three of the ^3P states that are easy to recognize, $|p_1\ p_0\ |$, $|p_1\ p_{-1}\ |$, and $|p_{-1}\ p_0\ |$, we apply S_- to obtain the $M_S=0$ functions:

$$S_-\ ^3P(M_L=1, M_S=1) = [S_-(1) + S_-(2)] \qquad |p_1\ p_0\ |$$

$$= \hbar(1(2)-1(0))^{1/2}\ ^3P(M_L=1, M_S=0)$$

$$= \hbar(1/2(3/2)-1/2(-1/2))^{1/2}\ |p_1\ p_0\ | + \hbar(1)^{1/2}\ |p_1\ p_0\ |,$$

so,

$$^3P(M_L=1, M_S=0) = 2^{-1/2}\ [|p_1\ p_0\ | + |p_1\ p_0\ |].$$

The same process applied to $|p_1\ p_{-1}\ |$ and $|p_{-1}\ p_0\ |$ gives

$$1/\ 2[||p_1\ p_{-1}\ | + |p_1\ p_{-1}\ |]\ \text{and}\ 1/\ 2[||p_{-1}\ p_0\ | + |p_{-1}\ p_0\ |],$$

respectively.

The $^3P(M_L=1, M_S=0) = 2^{-1/2}\ [|p_1\ p_0\ | + |p_1\ p_0\ |$ function can be acted on with L_- to generate $^3P(M_L=0, M_S=0)$:

$$L_-\ ^3P(M_L=1, M_S=0) = [L_-(1) + L_-(2)]\ 2^{-1/2}\ [|p_1\ p_0\ | + |p_1\ p_0\ |]$$

$$= \hbar(1(2)-1(0))^{1/2}\ ^3P(M_L=0, M_S=0)$$

$$= \hbar(1(2)-1(0))^{1/2}\ 2^{-1/2}\ [|p_0\ p_0\ | + |p_0\ p_0\ |]$$

$$+ \hbar\ (1(2)-0(-1))^{1/2}\ 2^{-1/2}\ [|p_1\ p_{-1}\ | + |p_1\ p_{-1}\ |],$$

so,

$$^3P(M_L=0, M_S=0) = 2^{-1/2}\ [|p_1\ p_{-1}\ | + |p_1\ p_{-1}\ |].$$

The ^{1}D term symbol is handled in like fashion. Beginning with the $M_L = 2$ state $|p_1 \ p_1 \ |$, one applies L_- to generate the $M_L = 1$ state:

$L_- \ ^1D(M_L=2, M_S=0) = [L_-(1) + L_-(2)] \ |p_1 \ p_1 \ |$

$= \hbar(2(3)-2(1))^{1/2} \ ^1D(M_L=1, M_S=0)$

$= \hbar(1(2)-1(0))^{1/2} \ [|p_0 \ p_1 \ | + |p_1 \ p_0 \ |],$

so,

$^1D(M_L=1, M_S=0) = 2^{-1/2} \ [|p_0 \ p_1 \ | + |p_1 \ p_0 \ |].$

Applying L_- once more generates the $^1D(M_L=0, M_S=0)$ state:

$L_- \ ^1D(M_L=1, M_S=0) = [L_-(1) + L_-(2)] \ 2^{-1/2} \ [|p_0 \ p_1 \ | + |p_1 \ p_0 \ |]$

$= \hbar(2(3)-1(0))^{1/2} \ ^1D(M_L=0, M_S=0)$

$= \hbar(1(2)-0(-1))^{1/2} \ 2^{-1/2} \ [|p_{-1} \ p_1 \ | + |p_1 \ p_{-1} \ |]$

$\quad\quad + \hbar(1(2)-1(0))^{1/2} \ 2^{-1/2} \ [|p_0 \ p_0 \ | + |p_0 \ p_0 \ |],$

so,

$^1D(M_L=0, M_S=0) = 6^{-1/2}[\ 2|p_0 \ p_0 \ | + |p_{-1} \ p_1 \ | + |p_1 \ p_{-1} \ |].$

Notice that the $M_L=0$, $M_S=0$ states of ^3P and of ^1D are given in terms of the three determinants that appear in the "center" of the p^2 box diagram:

$^1D(M_L=0, M_S=0) = 6^{-1/2}[\ 2|p_0 \ p_0 \ | + |p_{-1} \ p_1 \ | + |p_1 \ p_{-1} \ |],$

$^3P(M_L=0, M_S=0) = 2^{-1/2} \ [|p_1 \ p_{-1} \ | + |p_1 \ p_{-1} \ |]$

$\quad\quad\quad = 2^{-1/2} \ [\ -|p_{-1} \ p_1 \ | + |p_1 \ p_{-1} \ |].$

The only state that has eluded us thus far is the ^1S state, which also has $M_L=0$ and $M_S=0$. To construct this state, which must also be some combination of the three determinants with $M_L=0$ and $M_S=0$, we use the fact that the ^1S wavefunction <u>must</u> be orthogonal to the

^{3}P and ^{1}D functions because ^{1}S, ^{3}P, and ^{1}D are eigenfunctions of the hermitian operator L^2 having different eigenvalues. The state that is normalized and is a combination of $|p_0 \ p_0|$, $|p_{-1} \ p_1|$, and $|p_1 \ p_{-1}|$ is given as follows:

$$^1S = 3^{-1/2} \left[|p_0 \ p_0| - |p_{-1} \ p_1| - |p_1 \ p_{-1}| \right].$$

The procedure used here to form the ^{1}S state illustrates point 3 in the above prescription for determining wavefunctions. Additional examples for constructing wavefunctions for atoms are provided later in this chapter and in Appendix G.

D. Inversion Symmetry

One more quantum number, that relating to the inversion (i) symmetry operator can be used in atomic cases because the total potential energy V is unchanged when <u>all</u> of the electrons have their position vectors subjected to inversion (i $\mathbf{r} = -\mathbf{r}$). This quantum number is straightforward to determine. Because each L, S, M_L, M_S, H state discussed above consist of a few (or, in the case of configuration interaction several) symmetry adapted combinations of Slater determinant functions, the effect of the inversion operator on such a wavefunction   can be determined by:

(i) applying i to each orbital occupied in   thereby generating a $\pm$ 1 factor for each orbital (+1 for s, d, g, i, etc orbitals; -1 for p, f, h, j, etc orbitals),

(ii) multiplying these $\pm$ 1 factors to produce an overall sign for the character of   under i.

When this overall sign is positive, the function   is termed "even" and its term symbol is appended with an "e" superscript (e.g., the ^{3}P level of the O atom, which has $1s^22s^22p^4$ occupancy is labeled $^3P^e$); if the sign is negative   is called "odd" and the term symbol is so amended (e.g., the ^{3}P level of $1s^22s^12p^1$ B$^+$ ion is labeled $^3P^o$).

E. Review of Atomic Cases

The orbitals of an atom are labeled by l and m quantum numbers; the orbitals belonging to a given energy and l value are 2l+1- fold degenerate. The many-electron Hamiltonian, H, of an atom and the antisymmetrizer operator $A = (1/N!) \sum_p s_p P$ commute with total $L_z = \sum_i L_z(i)$, as in the linear-molecule case. The additional symmetry present in the spherical atom reflects itself in the fact that L_x, and L_y now also commute with H and A. However, since L_z does not commute with L_x or L_y, new quantum

numbers can not be introduced as symmetry labels for these other components of **L**. A new symmetry label does arise when $L^2 = L_z^2 + L_x^2 + L_y^2$ is introduced; L^2 commutes with H, A , and L_z, so proper eigenstates (and trial wavefunctions) can be labeled with L, M_L, S, M_s, and H quantum numbers.

To identify the states which arise from a given atomic configuration and to construct properly symmetry-adapted determinental wave functions corresponding to these symmetries, one must employ L and M_L and S and M_S angular momentum tools. One first identifies those determinants with maximum M_S (this then defines the maximum S value that occurs); within that set of determinants, one then identifies the determinant(s) with maximum M_L (this identifies the highest L value). This determinant has S and L equal to its M_s and M_L values (this can be verified, for example for L, by acting on this determinant with L^2 in the form

$$L^2 = L_-L_+ + L_z^2 + \hbar L_z$$

and realizing that L_+ acting on the state must vanish); other members of this L,S energy level can be constructed by sequential application of S_- and $L_- = \sum_i L_-(i)$. Having exhausted a set of (2L+1)(2S+1) combinations of the determinants belonging to the given configuration, one proceeds to apply the same procedure to the remaining determinants (or combinations thereof). One identifies the maximum M_S and, within it, the maximum M_L which thereby specifies another S, L label and a new "maximum" state. The determinental functions corresponding to these L,S (and various M_L, $M_{s\,)}$ values can be constructed by applying S_- and L_- to this "maximum" state. This process is continued until all of the states and their determinental wave functions are obtained.

As illustrated above, any p^2 configuration gives rise to $^3P^e$, $^1D^e$, and $^1S^e$ levels which contain nine, five, and one state respectively. The use of L and S angular momentum algebra tools allows one to identify the wavefunctions corresponding to these states. As shown in detail in Appendix G, in the event that spin-orbit coupling causes the Hamiltonian, **H,** not to commute with **L** or with **S** but only with their vector sum **J**= **L** + **S**, then these L^2 S^2 L_z S_z eigenfunctions must be coupled (i.e., recombined) to generate J^2 J_z eigenstates. The steps needed to effect this coupling are developed and illustrated for the above p^2 configuration case in Appendix G.

In the case of a pair of non-equivalent p orbitals (e.g., in a $2p^13p^1$ configuration), even more states would arise. They can also be found using the tools provided above. Their symmetry labels can be obtained by vector coupling (see Appendix G) the spin and orbital angular momenta of the two subsystems. The orbital angular momentum coupling

with $l = 1$ and $l = 1$ gives $L = 2$, 1, and 0 or D, P, and S states. The spin angular momentum coupling with $s = 1/2$ and $s = 1/2$ gives $S = 1$ and 0, or triplet and singlet states. So, vector coupling leads to the prediction that $^3D^e$, $^1D^e$, $^3P^e$, $^1P^e$, $^3S^e$, and $^1S^e$ states can be formed from a pair of non-equivalent p orbitals. It is seen that more states arise when non-equivalent orbitals are involved; for equivalent orbitals, some determinants vanish, thereby decreasing the total number of states that arise.

III. Linear Molecule Term Symbols and Wavefunctions

A. Non-Equivalent Orbital Term Symbols

Equivalent angular momenta arising in linear molecules also require use of specialized angular momentum coupling. Their spin angular momenta are coupled exactly as in the atomic case because both for atoms and linear molecules, S^2 and S_z commute with H. However, unlike atoms, linear molecules no longer permit L^2 to be used as an operator that commutes with H; L_z still does, but L^2 does not. As a result, when coupling non-equivalent linear molecule angular momenta, one vector couples the electron spins as before. However, in place of vector coupling the individual orbital angular momenta, one adds the individual L_z values to obtain the L_z values of the coupled system. For example, the $\pi^1 \pi'^1$ configuration gives rise to $S=1$ and $S=0$ spin states. The individual m_l values of the two pi-orbitals can be added to give $M_L = 1+1$, 1-1, -1+1, and -1-1, or 2, 0, 0, and -2. The $M_L = 2$ and -2 cases are degenerate (just as the $m_l = 2$ and -2 orbitals are and the $m_l = 1$ and -1 orbitals are) and are denoted by the term symbol Δ; there are two distinct $M_L = 0$ states that are denoted Σ. Hence, the $\pi^1 \pi'^1$ configuration yields $^3\Delta$, $^3\Sigma$, $^3\Sigma$, $^1\Delta$, $^1\Sigma$, and $^1\Sigma$ term symbols.

B. Equivalent-Orbital Term Symbols

To treat the equivalent-orbital case π^2, one forms a box diagram as in the atom case:

M_L	2	1	0
M_S \quad 1			$|\pi_1 \quad \pi_{-1}|$
0	$|\pi_1 \quad \bar{\pi}_1|$		$|\pi_1 \quad \bar{\pi}_{-1}|$,

| -1   1 |

The process is very similar to that used for atoms. One first identifies the highest M_S value (and hence an S value that occurs) and <u>within</u> that M_S, the highest M_L. However, the highest M_L does <u>not</u> specify an L-value, because L is no longer a "good quantum number" because L^2 no longer commutes with H. Instead, we simply take the highest M_L value (and minus this value) as specifying a , , , , , etc. term symbol. In the above example, the highest M_S value is $M_S = 1$, so there is an S = 1 level. Within $M_S = 1$, the highest $M_L = 0$; hence, there is a ^{3} level.

After deleting from the box diagram entries corresponding to M_S values ranging from -S to S and M_L values of M_L and - M_L, one has (again using italics to denote the deleted entries):

M_L	2	1	0
M_S 1			/ *1* *-1* /
0	| 1 1 |		/ *1* *-1* /,
			| -1 1 |

Among the remaining entries, the highest M_S value is $M_S = 0$, and within this M_S the highest M_L is $M_L = 2$. Thus, there is a ^{1} state. Deleting entries with $M_S = 0$ and $M_L = 2$ and -2, one has left the following box diagram:

M_L	2	1	0
M_S 1			/ *1* *-1* /
0	/ *1* *1* /		/ *1* *-1* /,
			| -1 1 |

There still remains an entry with $M_S = 0$ and $M_L = 0$; hence, there is also a ^{1} level.

Recall that the non-equivalent ^{1} ' ^{1} case yielded ^{3} , ^{3} , ^{3} , ^{1} , ^{1} , and ^{1} term symbols. The equivalent ^{2} case yields only ^{3} , ^{1} , and ^{1} term symbols. Again,

whenever one is faced with equivalent angular momenta in a linear-molecule case, one must use the box method to determine the allowed term symbols. If one has a mixture of equivalent and non-equivalent angular momenta, it is possible to treat the equivalent angular momenta using boxes and to then add in the non-equivalent angular momenta using the more straightforward technique. For example, the $\pi^2\sigma^1$ configuration can be treated by coupling the π^2 as above to generate $^3\Sigma$, $^1\Delta$, and $^1\Sigma$ and then vector coupling the spin of the third electron and additively coupling the $m_l = 2$ and -2 of the third orbital. The resulting term symbols are $^4\Sigma$, $^2\Sigma$, $^2\Sigma$, $^2\Delta$, $^2\Gamma$, and $^2\Sigma$ (e.g., for the $^1\Delta$ intermediate state, adding the δ orbital's m_l values gives total M_L values of $M_L = 2+2$, $2-2$, $-2+2$, and $-2-2$, or 4, 0, 0, and -4).

C. Linear-Molecule Configuration Wavefunctions

Procedures analogous to those used for atoms can be applied to linear molecules. However, in this case only $S_\pm$ can be used; $L_\pm$ no longer applies because L is no longer a good quantum number. One begins as in the atom case by identifying determinental functions for which M_L and M_S are unique. In the π^2 example considered above, these states include $|\pi_1\alpha\ \pi_{-1}\alpha|$, $|\pi_1\alpha\ \pi_1\beta|$, and their mirror images. These states are members of the $^3\Sigma$ and $^1\Delta$ levels, respectively, because the first has $M_S=1$ and because the latter has $M_L = 2$.

Applying S_- to this $^3\Sigma$ state with $M_S=1$ produces the $^3\Sigma$ state with $M_S = 0$:

$$S_-\ ^3\Sigma\ (M_L=0,\ M_S=1) = [S_-(1) + S_-(2)]\ |\pi_1\alpha\ \pi_{-1}\alpha|$$

$$= \hbar(1(2)-1(0))^{1/2}\ ^3\Sigma\ (M_L=0,\ M_S=0)$$

$$= \hbar\ (1)^{1/2}\ [|\pi_1\alpha\ \pi_{-1}\beta| + |\pi_1\beta\ \pi_{-1}\alpha|],$$

so,

$$^3\Sigma\ (M_L=0,\ M_S=0) = 2^{-1/2}\ [|\pi_1\alpha\ \pi_{-1}\beta| + |\pi_1\beta\ \pi_{-1}\alpha|].$$

The only other state that can have $M_L=0$ and $M_S=0$ is the $^1\Sigma$ state, which must itself be a combination of the two determinants, $|\pi_1\alpha\ \pi_{-1}\beta|$ and $|\pi_1\beta\ \pi_{-1}\alpha|$, with $M_L=0$ and $M_S=0$. Because the $^1\Sigma$ state has to be orthogonal to the $^3\Sigma$ state, the combination must be

$$^1\Sigma = 2^{-1/2}\ [|\pi_1\alpha\ \pi_{-1}\beta| - |\pi_1\beta\ \pi_{-1}\alpha|].$$

As with the atomic systems, additional examples are provided later in this chapter and in Appendix G.

D. Inversion Symmetry and σ_v Reflection Symmetry

For homonuclear molecules (e.g., O_2, N_2, etc.) the inversion operator i (where inversion of all electrons now takes place through the center of mass of the nuclei rather than through an individual nucleus as in the atomic case) is also a valid symmetry, so wavefunctions Ψ may also be labeled as even or odd. The former functions are referred to as **gerade** (g) and the latter as **ungerade** (u) (derived from the German words for even and odd). The g or u character of a term symbol is straightforward to determine. Again one

(i) applies i to each orbital occupied in Ψ thereby generating a ± 1 factor for each orbital (+1 for σ, σ^*, π, π^*, etc orbitals; -1 for σ^*, π, π^*, δ, etc orbitals),

(ii) multiplying these ± 1 factors to produce an overall sign for the character of Ψ under i.

When this overall sign is positive, the function Ψ is gerade and its term symbol is appended with a "g" subscript (e.g., the $^3\Sigma$ level of the O_2 molecule, which has $\pi_u^4\pi_g^{*2}$ occupancy is labeled $^3\Sigma_g$); if the sign is negative, Ψ is ungerade and the term symbol is so amended (e.g., the $^3\Sigma$ level of the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 1\sigma_u^1$ configuration of the Li_2 molecule is labeled $^3\Sigma_u$).

Finally, for linear molecules in Σ states, the wavefunctions can be labeled by one additional quantum number that relates to their symmetry under reflection of <u>all</u> electrons through a σ_v plane passing through the molecule's C_∞ axis. If Ψ is even, a + sign is appended as a superscript to the term symbol; if Ψ is odd, a - sign is added.

To determine the σ_v symmetry of Ψ, one first applies σ_v to each orbital in Ψ. Doing so replaces the azimuthal angle ϕ of the electron in that orbital by $2\pi - \phi$; because orbitals of linear molecules depend on ϕ as $\exp(im\phi)$, this changes the orbital into $\exp(im(-\phi))\exp(2\pi im) = \exp(-im\phi)$. In effect, σ_v applied to Ψ changes the signs of all of the m values of the orbitals in Ψ. One then determines whether the resultant $\sigma_v\Psi$ is equal to or opposite in sign from the original Ψ by inspection. For example, the $^3\Sigma_g$ ground state of O_2, which has a Slater determinant function

$|S=1, M_S=1> = | \pi^*_1 \alpha \pi^*_{-1}\alpha |$

$= 2^{-1/2} [\pi^*_1(\mathbf{r_1}) \alpha_1 \pi^*_{-1}(\mathbf{r_2}) \alpha_2 - \pi^*_1(\mathbf{r_2}) \alpha_2 \pi^*_{-1}(\mathbf{r_1}) \alpha_1].$

Recognizing that $\sigma_v \phi^*_1 = \phi^*_{-1}$ and $\sigma_v \phi^*_{-1} = \phi^*_1$, then gives

$$\sigma_v |S=1, M_S=1> = | \phi^*_1 \alpha \quad \phi^*_{-1} \alpha |$$

$$= 2^{-1/2} [\phi^*_{-1}(\mathbf{r_1}) \alpha_1 \phi^*_1(\mathbf{r_2}) \alpha_2 - \phi^*_{-1}(\mathbf{r_2}) \alpha_2 \phi^*_1(\mathbf{r_1}) \alpha_1]$$

$$= (-1) 2^{-1/2} [\phi^*_1(\mathbf{r_1}) \alpha_1 \phi^*_{-1}(\mathbf{r_2}) \alpha_2 - \phi^*_1(\mathbf{r_2}) \alpha_2 \phi^*_{-1}(\mathbf{r_1}) \alpha_1],$$

so this wavefunction is odd under σ_v which is written as $^3\Sigma_g^-$.

E. Review of Linear Molecule Cases

Molecules with axial symmetry have orbitals of σ, π, δ, ϕ, etc symmetry; these orbitals carry angular momentum about the z-axis in amounts (in units of $\hbar$) 0, +1 and -1, +2 and -2, +3 and -3, etc. The axial point-group symmetries of configurations formed by occupying such orbitals can be obtained by adding, in all possible ways, the angular momenta contributed by each orbital to arrive at a set of possible total angular momenta. The eigenvalue of total $L_z = \sum_i L_z(i)$ is a valid quantum number because total L_z commutes with the Hamiltonian and with P_{ij}; one obtains the eigenvalues of total L_z by adding the individual spin-orbitals' m eigenvalues because of the additive form of the L_z operator. L^2 no longer commutes with the Hamiltonian, so it is no longer appropriate to construct N-electron functions that are eigenfunctions of L^2. Spin symmetry is treated as usual via the spin angular momentum methods described in the preceding sections and in Appendix G. For molecules with centers of symmetry (e.g., for homonuclear diatomics or ABA linear triatomics), the many-electron spin-orbital product inversion symmetry, which is equal to the product of the individual spin-orbital inversion symmetries, provides another quantum number with which the states can be labeled. Finally the σ_v symmetry of Σ states can be determined by changing the m values of all orbitals in Σ and then determining whether the resultant function is equal to Σ or to $-\Sigma$.

If, instead of a π^2 configuration like that treated above, one had a δ^2 configuration, the above analysis would yield $^1\Gamma$, $^1\Sigma$ and $^3\Sigma$ symmetries (because the two δ orbitals' m values could be combined as 2 + 2, 2 - 2 , -2 + 2, and -2 -2); the wavefunctions would be identical to those given above with the π_1 orbitals replaced by δ_2 orbitals and π_{-1} replaced by δ_{-2}. Likewise, ϕ^2 gives rise to ^1I, $^1\Sigma$, and $^3\Sigma$ symmetries.

For a ^{1} $'^1$ configuration in which two non-equivalent   orbitals (i.e., orbitals which are of   symmetry but which are not both members of the same degenerate set; an example would be the   and   * orbitals in the B_2 molecule) are occupied, the above analysis must be expanded by including determinants of the form: | $_1$ $'_1$ |, | $_{-1}$ $'_{-1}$ |, | $_1$ $'_1$ |, | $_{-1}$ $'_{-1}$ |. Such determinants were excluded in the ^{2} case because they violated the Pauli principle (i.e., they vanish identically when ' =). Determinants of the form | $'_1$ $_{-1}$ |, | $'_1$ $_1$ |, | $'_{-1}$ $_{-1}$ |, | $'_1$ $_{-1}$ |, | $'_1$ $_{-1}$ |, and | $'_1$ $_{-1}$ | are now distinct and must be included as must the determinants | $_1$ $'_{-1}$ |, | $_1$ $'_1$ |, | $_{-1}$ $'_{-1}$ |, | $_1$ $'_{-1}$ |, | $_1$ $'_{-1}$ |, and | $_1$ $'_{-1}$ |, which are analogous to those used above. The result is that there are more possible determinants in the case of non-equivalent orbitals. However, the techniques for identifying space-spin symmetries and creating proper determinental wavefunctions are the same as in the equivalent-orbital case.

For any ^{2} configuration, one finds ^{1} , ^{1} , and ^{3} wavefunctions as detailed earlier; for the ^{1} $'^1$ case, one finds ^{3} , ^{1} , ^{3} , ^{1} , ^{3} , and ^{1} wavefunctions by starting with the determinants with the maximum M_s value, identifying states by their $|M_L|$ values, and using spin angular momentum algebra and orthogonality to generate states with lower M_s and, subsequently, lower S values. Because L^2 is not an operator of relevance in such cases, raising and lowering operators relating to **L** are <u>not</u> used to generate states with lower   values. States with specific   values are formed by occupying the orbitals in all possible manners and simply computing   as the absolute value of the sum of the individual orbitals' m-values.

If a center of symmetry is present, all of the states arising from ^{2} are gerade; however, the states arising from ^{1} $'^1$ can be gerade if   and   ' are both g or both u or ungerade if   and   ' are of opposite inversion symmetry.

The state symmetries appropriate to the non-equivalent ^{1} $'^1$ case can, alternatively, be identified by "coupling" the spin and L_z angular momenta of two "independent" subsystems-the ^{1} system which gives rise to ^{2} symmetry (with M_L =1 and -1 and S =1/2) and the $'^1$ system which also give ^{2} symmetry. The coupling gives rise to triplet and singlet spins (whenever two full vector angular momenta | j,m> and | j',m'> are coupled, one can obtain total angular momentum values of J =j+j', j+j'-1, j+j'-2,... |j-j'|; see Appendix G for details) and to M_L values of 1+1=2, -1-1=-2, 1-1=0 and -1+1=0 (i.e., to , , and   states). The L_z angular momentum coupling is <u>not</u> carried out in the full vector coupling scheme used for the electron spins because, unlike the spin case where one is forming eigenfunctions of total S^2 and S_z, one is only forming L_z eigenstates (i.e., L^2 is not a valid quantum label). In the case of axial angular momentum coupling, the various possible M_L values of each subsystem are added to those of the other subsystem to

arrive at the total M_L value. This angular momentum coupling approach gives the same set of symmetry labels ($^3\Sigma$, $^1\Sigma$, $^3\Delta$, $^1\Delta$, $^3\Sigma$, and $^1\Sigma$) as are obtained by considering all of the determinants of the composite system as treated above.

IV. Non-Linear Molecule Term Symbols and Wavefunctions

A. Term Symbols for Non-Degenerate Point Group Symmetries

The point group symmetry labels of the individual orbitals which are occupied in any determinental wave function can be used to determine the overall spatial symmetry of the determinant. When a point group symmetry operation is applied to a determinant, it acts on all of the electrons in the determinant; for example, $\sigma_v|\phi_1\phi_2\phi_3|=|\sigma_v\phi_1 \sigma_v\phi_2 \sigma_v\phi_3|$. If each of the spin-orbitals ϕ_i belong to non-degenerate representations of the point group, $\sigma_v\phi_i$ will yield the character $\chi_i(\sigma_v)$ appropriate to that spin-orbital multiplying ϕ_i. As a result, $\sigma_v|\phi_1\phi_2\phi_3|$ will equal the product of the three characters (one for each spin-orbital) $\prod_i \chi_i(\sigma_v)$ times $|\phi_1\phi_2\phi_3|$. This gives an example of how the symmetry of a spin-orbital product (or an antisymmetrized product) is given as the <u>direct product</u> of the symmetries of the individual spin-orbitals in the product; the point group symmetry operator, because of its product nature, passes through or commutes with the antisymmetrizer. It should be noted that any closed-shell parts of the determinant (e.g.,$1a_1^2 2a_1^2 1b_2^2$ in the configuration $1a_1^2 2a_1^2 1b_2^2\, 1b_1^1$) contribute unity to the direct product because the squares of the characters of any non-degenerate point group for any group operation equals unity. Therefore, only the open-shell parts need to be considered further in the symmetry analysis. For a brief introduction to point group symmetry and the use of direct products in this context, see Appendix E.

An example will help illustrate these ideas. Consider the formaldehyde molecule H_2CO in C_{2v} symmetry. The configuration which dominates the ground-state wavefunction has doubly occupied O and C 1s orbitals, two CH bonds, a CO σ bond, a CO π bond, and two O-centered lone pairs; this configuration is described in terms of symmetry adapted orbitals as follows: $(1a_1^2 2a_1^2 3a_1^2 1b_2^2$ $4a_1^2 1b_1^2 5a_1^2 2b_2^2)$ and is of $^1A_1$ symmetry because it is entirely closed-shell (note that lower case letters are used to denote the symmetries of orbitals and capital letters are used for many-electron functions' symmetries).

The lowest-lying n=> π^* states correspond to a configuration (only those orbitals whose occupancies differ from those of the ground state are listed) of the form $2b_2^1 2b_1^1$, which gives rise to $^1A_2$ and $^3A_2$ wavefunctions (the direct product of the open-shell spin

orbitals is used to obtain the symmetry of the product wavefunction: $A_2 = b_1 \times b_2$). The $\pi \Rightarrow \pi^*$ excited configuration $1b_1^1 2b_1^1$ gives $^1A_1$ and $^3A_1$ states because $b_1 \times b_1 = A_1$.

The only angular momentum coupling that occurs in non-linear molecules involves the electron spin angular momenta, which are treated in a vector coupling manner. For example, in the lowest-energy state of formaldehyde, the orbitals are occupied in the configuration $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^2 5a_1^2 2b_2^2$. This configuration has only a single entry in its "box". Its highest M_S value is $M_S = 0$, so there is a singlet $S = 0$ state. The spatial symmetry of this singlet state is totally symmetric A_1 because this is a closed-shell configuration.

The lowest-energy $n \to \pi^*$ excited configuration of formaldehyde has a $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^2 5a_1^2 2b_2^1 2b_1^1$ configuration, which has a total of four entries in its "box" diagram:

$$M_S = 1 \qquad |2b_2^1 \ \ 2b_1^1 \ |,$$
$$M_S = 0 \qquad |2b_2^1 \ \ \overline{2b_1^1} \ |,$$
$$M_S = 0 \qquad |\overline{2b_2^1} \ 2b_1^1 \ |,$$
$$M_S = -1 \qquad |\overline{2b_2^1} \ \ \overline{2b_1^1} \ |.$$

The highest M_S value is $M_S = 1$, so there is an $S = 1$ state. After deleting one entry each with $M_S = 1$, 0, and -1, there is one entry left with $M_S = 0$. Thus, there is an $S = 0$ state also.

As illustrated above, the spatial symmetries of these four $S = 1$ and $S = 0$ states are obtained by forming the direct product of the "open-shell" orbitals that appear in this configuration: $b_2 \times b_1 = A_2$.
All four states have this spatial symmetry. In summary, the above configuration yields $^3A_2$ and $^1A_2$ term symbols. The $\pi \to \pi^{*1}$ configuration $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^1 5a_1^2 2b_2^2 2b_1^1$ produces $^3A_1$ and $^1A_1$ term symbols (because $b_1 \times b_1 = A_1$).

B. Wavefunctions for Non-Degenerate Non-Linear Point Molecules

The techniques used earlier for linear molecules extend easily to non-linear molecules. One begins with those states that can be straightforwardly identified as unique entries within the box diagram. For polyatomic molecules with no degenerate representations, the spatial symmetry of each box entry is identical and is given as the direct product of the open-shell orbitals. For the formaldehyde example considered earlier, the spatial symmetries of the $n \to \pi^*$ and $\pi \to \pi^*$ states were A_2 and A_1, respectively.

After the unique entries of the box have been identified, one uses $S_\pm$ operations to find the other functions. For example, the wavefunctions of the $^3A_2$ and $^1A_2$ states of the nπ* $1a_1^2 2a_1^2 3a_1^2 1b_2^2 4a_1^2 1b_1^2 5a_1^2 2b_2^1 2b_1^1$ configuration of formaldehyde are formed by first identifying the $M_S = \pm 1$ components of the S = 1 state as $|2b_2\ \alpha\ 2b_1\ \alpha\ |$ and $|2b_2\ \beta\ 2b_1\ \beta\ |$ (all of the closed-shell components of the determinants are not explicitly given). Then, applying S_- to the $M_S = 1$ state, one obtains the $M_S = 0$ component $(1/2)^{1/2}$ $[|2b_2\ \alpha\ 2b_1\ \beta\ | + |2b_2\ \beta\ 2b_1\ \alpha\ |]$. The singlet state is then constructed as the combination of the two determinants appearing in the S = 1, $M_S = 0$ state that is orthogonal to this triplet state. The result is $(1/2)^{1/2}$ $[|2b_2\ \alpha\ 2b_1\ \beta\ | - |2b_2\ \beta\ 2b_1\ \alpha\ |]$.

The results of applying these rules to the nπ* and $\pi\pi$* states are as follows:

$^3A_2$ $(M_s = 1) = |1a_1\ \alpha\ 1a_1\ \beta\ 2a_1\ \alpha\ 2a_1\ \beta\ 3a_1\ \alpha\ 3a_1\ \beta\ 1b_2\ \alpha\ 1b_2\ \beta\ 4a_1\ \alpha\ 4a_1\ \alpha\ 1\ \alpha\ 1\ \beta\ 1b_1\ \alpha$

$ 5a_1\ \alpha\ 5a_1\ \beta\ 2b_2\ \alpha\ 2b_1\ \alpha\ |$,

$^3A_2$ $(M_s = 0) = 1/\sqrt{2}\ [|2b_2\ \alpha\ 2b_1\ \beta\ | + |2b_2\ \beta\ 2b_1\ \alpha\ |]$,

$^3A_2$ $(M_S = -1) = |2b_2\ \beta\ 2b_1\ \beta\ |$,
$^1A_2 = 1/\sqrt{2}\ [|2b_2\ \alpha\ 2b_1\ \beta\ | - |2b_2\ \beta\ 2b_1\ \alpha\ |]$.

The lowest $\pi\pi$* states of triplet and singlet spin involve the following:

$^3A_1$ $(M_s = 1) = |1b_1\ \alpha\ 2b_1\ \alpha\ |$,

$^1A_1 = 1/\sqrt{2}\ [|1b_1\ \alpha\ 2b_1\ \beta\ | - |1b_1\ \beta\ 2b_1\ \alpha\ |]$.

In summary, forming spatial- and spin- adapted determinental functions for molecules whose point groups have no degenerate representations is straightforward. The direct product of all of the open-shell spin orbitals gives the point-group symmetry of the determinant. The spin symmetry is handled using the spin angular momentum methods introduced and illustrated earlier.

C. Extension to Degenerate Representations for Non-Linear Molecules

Point groups in which degenerate orbital symmetries appear can be treated in like fashion but require more analysis because a symmetry operation R acting on a degenerate

orbital generally yields a linear combination of the degenerate orbitals rather than a multiple of the original orbital (i.e., $R \, \phi_i = \chi_i(R) \, \phi_i$ is no longer valid). For example, when a pair of degenerate orbitals (denoted e_1 and e_2) are involved, one has

$$R \, e_i = \sum_j R_{ij} \, e_j,$$

where R_{ij} is the 2x2 matrix representation of the effect of R on the two orbitals. The effect of R on a product of orbitals can be expressed as:

$$R \, e_i e_j = \sum_{k,l} R_{ik} R_{jl} \, e_k e_l .$$

The matrix $R_{ij,kl} = R_{ik} R_{jl}$ represents the effect of R on the orbital products in the same way R_{ik} represents the effect of R on the orbitals. One says that the orbital products also form a basis for a representation of the point group. The character (i.e., the trace) of the representation matrix $R_{ij,kl}$ appropriate to the orbital product basis is seen to equal the product of the characters of the matrix R_{ik} appropriate to the orbital basis: $\chi_e^2(R) = \chi_e(R) \, \chi_e(R)$, which is, of course, why the term "direct product" is used to describe this relationship.

For point groups which contain no degenerate representations, the direct product of one symmetry with another is equal to a unique symmetry; that is, the characters $\chi(R)$ obtained as $\chi_a(R) \, \chi_b(R)$ belong to a pure symmetry and can be immediately identified in a point-group character table. However, for point groups in which degenerate representations occur, such is not the case. The direct product characters will, in general, not correspond to the characters of a single representation; they will contain contributions from more than one representation and these contributions will have to be sorted out using the tools provided below.

A concrete example will help clarify these concepts. In C_{3v} symmetry, the orbitals of the cyclopropenyl anion transform according to a_1 and e symmetries

a_1 e_1 e_2
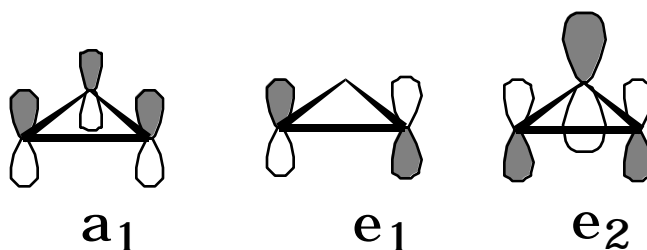
and can be expressed as LCAO-MO's in terms of the individual p_i orbitals as follows:

$$a_1 = 1/\sqrt{3}\,[\,p_1 + p_2 + p_3\,],\quad e_1 = 1/\sqrt{2}\,[\,p_1 - p_3\,],$$

and

$$e_2 = 1/\sqrt{6}\,[\,2\,p_2 - p_1 - p_3\,].$$

For the anion's lowest energy configuration, the orbital occupancy $a_1^2 e^2$ must be considered, and hence the spatial and spin symmetries arising from the e^2 configuration are of interest. The character table shown below

C_{3v}	E	$3\sigma_v$	$2 C_3$
a_1	1	1	1
a_2	1	-1	1
e	2	0	-1

allows one to compute the characters appropriate to the direct product (e x e) as $\chi(E) = 2\mathrm{x}2 = 4$, $\chi(\sigma_v) = 0\mathrm{x}0 = 0$, $\chi(C_3) = (-1)\mathrm{x}(-1) = 1$.

This reducible representation (the occupancy of two e orbitals in the anion gives rise to more than one state, so the direct product e x e contains more than one symmetry component) can be decomposed into pure symmetry components (labels Γ are used to denote the irreducible symmetries) by using the decomposition formula given in Appendix E:

$$n(\Gamma) = 1/g\ \sum_R \chi(R)\ \chi_\Gamma(R).$$

Here g is the order of the group (the number of symmetry operations in the group- 6 in this case) and $\chi(R)$ is the character for the particular symmetry Γ whose component in the direct product is being calculated.

For the case given above, one finds $n(a_1) = 1$, $n(a_2) = 1$, and $n(e) = 1$; so within the configuration e^2 there is one A_1 wavefunction, one A_2 wavefunction and a pair of E wavefunctions (where the symmetry labels now refer to the symmetries of the determinental wavefunctions). This analysis tells one how many different wavefunctions of various spatial symmetries are contained in a configuration in which degenerate orbitals are fractionally occupied. Considerations of spin symmetry and the construction of proper determinental wavefunctions, as developed earlier in this Section, still need to be applied to each spatial symmetry case.

To generate the proper A_1, A_2, and E wavefunctions of singlet and triplet spin symmetry (thus far, it is not clear which spin can arise for each of the three above spatial symmetries; however, only singlet and triplet spin functions can arise for this two-electron example), one can apply the following (un-normalized) symmetry projection operators (see **Appendix E** where these projectors are introduced) to all determinental wavefunctions arising from the e^2 configuration:

$$P_\Gamma = \sum_R \chi_\Gamma(R)\, R .$$

Here, $\chi_\Gamma(R)$ is the character belonging to symmetry Γ for the symmetry operation R. Applying this projector to a determinental function of the form $|\phi_i \phi_j|$ generates a sum of determinants with coefficients determined by the matrix representations R_{ik}:

$$P_\Gamma |\phi_i \phi_j| = \sum_R \sum_{kl} \chi_\Gamma(R)\, R_{ik} R_{jl} |\phi_k \phi_l|.$$

For example, in the e^2 case, one can apply the projector to the determinant with the maximum M_s value to obtain

$$P_\Gamma |e_1\alpha\ e_2\alpha| = \sum_R \chi_\Gamma(R)\, [R_{11}R_{22} |e_1\alpha\ e_2\alpha| + R_{12}R_{21} |e_2\alpha\ e_1\alpha|]$$

$$= \sum_R \chi_\Gamma(R)\, [R_{11}R_{22} - R_{12}R_{21}] |e_1\alpha\ e_2\alpha|,$$

or to the other two members of this triplet manifold, thereby obtaining

$$P_\Gamma |e_1\beta\ e_2\beta| = \sum_R \chi_\Gamma(R)\, [R_{11}R_{22} - R_{12}R_{21}] |e_1\beta\ e_2\beta|$$

and

$$P \quad 1/2 \, [|e_1 \ e_2 \ | + |e_1 \ e_2 \ |] = \sum_R \ (R) \, [R_{11}R_{22} - R_{12}R_{21}]$$

$$1/2[|e_1 \ e_2 \ | + |e_1 \ e_2 \ |] \ .$$

The other (singlet) determinants can be symmetry analyzed in like fashion and result in the following:

$$P \quad |e_1 \ e_1 \ | = \sum_R \ (R)\{R_{11}R_{11}|e_1 \ e_1 \ | + R_{12}R_{12} \, |e_2 \ e_2 \ | + R_{11}R_{12}$$
$$[|e_1 \ e_2 \ | - |e_1 \ e_2 \ |]\},$$

$$P \quad |e_2 \ e_2 \ | = \sum_R \ (R)\{R_{22}R_{22} \, |e_2 \ e_2 \ | + R_{21}R_{21}|e_1 \ e_1 \ | + R_{22}R_{21}$$
$$[|e_2 \ e_1 \ | - |e_2 \ e_1 \ |]\},$$

and

$$P \quad 1/2[|e_1 \ e_2 \ | - |e_1 \ e_2 \ |] = \sum_R \ (R) \, \{ \ 2 \, R_{11}R_{21}|e_1 \ e_1 \ |$$
$$+ \ 2 \, R_{22}R_{12}|e_2 \ e_2 \ | + (\, R_{11}R_{22} + R_{12}R_{21}) \, [|e_1 \ e_2 \ | - |e_1 \ e_2 \ |]\}.$$

To make further progress, one needs to evaluate the R_{ik} matrix elements for the particular orbitals given above and to then use these explicit values in the above equations. The matrix representations for the two e orbitals can easily be formed and are as follows:

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} -1/2 & 3/2 \\ 3/2 & 1/2 \end{pmatrix}$$

$$\mathrm{E} \qquad\qquad\qquad \mathrm{v} \qquad\qquad\qquad \mathrm{'v}$$

$$\begin{pmatrix} -1/2 & -3/2 \\ -3/2 & 1/2 \end{pmatrix} \begin{pmatrix} -1/2 & 3/2 \\ -3/2 & -1/2 \end{pmatrix} \begin{pmatrix} -1/2 & -3/2 \\ 3/2 & -1/2 \end{pmatrix}$$

$$\mathrm{''v} \qquad\qquad\qquad \mathrm{C}_3 \qquad\qquad\qquad \mathrm{C'}_3$$

.

Turning first to the three triplet functions, one notes that the effect of the symmetry projector acting on each of these three was the following multiple of the respective function:

$$\sum_R \ (R) \, [R_{11}R_{22}$$

-$R_{12}R_{21}$]. Evaluating this sum for each of the three symmetries Γ = A_1, A_2, and E, one obtains values of 0, 2, and 0 , respectively. That is, the projection of the each of the original triplet determinants gives zero except for A_2 symmetry. This allows one to conclude that there are no A_1 or E triplet functions in this case; the triplet functions are of pure $^3A_2$ symmetry.

Using the explicit values for R_{ik} matrix elements in the expressions given above for the projection of each of the singlet determinental functions, one finds only the following non-vanishing contributions:

(i) For A_1 symmetry- P |e_1 α e_1 β | = 3[|e_1 α e_1 β | + |e_2 α e_2 β |] = P |e_2 α e_2 β |,

(ii) For A_2 symmetry- all projections vanish,

(iii) For E symmetry- P |e_1 α e_1 β | = 3/2 [|e_1 α e_1 β | - |e_2 α e_2 β |] = -P |e_2 α e_2 β |

and P1/ $\surd$2[|e_1 α e_2 β | - |e_1 β e_2 α |] = 3 1/ $\surd$2[|e_1 α e_2 β | - |e_1 β e_2 α |].

Remembering that the projection process does not lead to a normalized function, although it does generate a function of pure symmetry, one can finally write down the normalized symmetry-adapted singlet functions as:

(i) $^1A_1$ = 1/ $\surd$2[|e_1 α e_1 β | + |e_2 α e_2 β |],

(ii) ^1E = { 1/ $\surd$2[|e_1 α e_1 β | - |e_2 α e_2 β |], and 1/ $\surd$2[|e_1 α e_2 β | - |e_1 β e_2 α |] }.

The triplet functions given above are:

(iii) $^3A_2$ = { |e_1 α e_2 α |, 1/ $\surd$2[|e_1 α e_2 β | +|e_1 β e_2 α |], and |e_1 β e_2 β | }.

In summary, whenever one has partially occupied degenerate orbitals, the characters corresponding to the direct product of the open-shell orbitals (as always, closed-shells contribute nothing to the symmetry analysis and can be ignored, although their presence must, of course, be specified when one finally writes down complete symmetry-adapted wavefunctions) must be reduced to identify the spatial symmetry components of the configuration. Given knowledge of the various spatial symmetries, one must then form determinental wavefunctions of each possible space and spin symmetry. In doing so, one

starts with the maximum M_S function and uses spin angular momentum algebra and orthogonality to form proper spin eigenfunctions, and then employs point group projection operators (which require the formation of the R_{ik} representation matrices). Antisymmetry, as embodied in the determinants, causes some space-spin symmetry combinations to vanish (e.g., $^3A_1$ and ^3E and $^1A_2$ in the above example) thereby enforcing the Pauli principle. This procedure, although tedious, is guaranteed to generate all space- and spin-symmetry adapted determinants for any configuration involving degenerate orbitals. The results of certain such combined spin and spatial symmetry analyses have been tabulated. For example, in Appendix 11 of Atkins such information is given in the form of tables of direct products for several common point groups.

For cases in which one has a <u>non-equivalent</u> set of degenerate orbitals (e.g., for a configuration whose open-shell part is $e^1e'^1$), the procedure is exactly the same as above except that the determination of the possible space-spin symmetries is more straightforward. In this case, singlet and triplet functions exist for all three space symmetries- A_1, A_2, and E, because the Pauli principle does not exclude determinants of the form $|e_1 \ e'_1 \ |$ or $|e_2 \ e'_2 \ |$, whereas the equivalent determinants ($|e_1 \ e_1 \ |$ or $|e_2 \ e_2 \ |$) vanish when the degenerate orbitals belong to the same set (in which case, one says that the orbitals are equivalent).

For all point, axial rotation, and full rotation group symmetries, this observation holds: if the orbitals are equivalent, certain space-spin symmetry combinations will vanish due to antisymmetry; if the orbitals are not equivalent, all space-spin symmetry combinations consistent with the content of the direct product analysis are possible. In either case, one must proceed through the construction of determinental wavefunctions as outlined above.

V. Summary

The ability to identify all term symbols and to construct all determinental wavefunctions that arise from a given electronic configuration is important. This knowledge allows one to understand and predict the changes (i.e., physical couplings due to external fields or due to collisions with other species and chemical couplings due to interactions with orbitals and electrons of a 'ligand' or another species) that each state experiences when the atom or molecule is subjected to some interaction. Such understanding plays central roles in interpreting the results of experiments in spectroscopy and chemical reaction dynamics.

The essence of this analysis involves being able to write each wavefunction as a combination of determinants each of which involves occupancy of particular spin-orbitals. Because different spin-orbitals interact differently with, for example, a colliding molecule, the various determinants will interact differently. These differences thus give rise to different interaction potential energy surfaces.

For example, the Carbon-atom $^3P(M_L=1, M_S=0) = 2^{-1/2} [|p_1 \ p_0 \ | + |p_1 \ p_0 \ |]$ and $^3P(M_L=0, M_S=0) = 2^{-1/2} [|p_1 \ p_{-1} \ | + |p_1 \ p_{-1} \ |]$ states interact quite differently in a collision with a closed-shell Ne atom. The $M_L = 1$ state's two determinants both have an electron in an orbital directed toward the Ne atom (the $2p_0$ orbital) as well as an electron in an orbital directed perpendicular to the C-Ne internuclear axis (the $2p_1$ orbital); the $M_L = 0$ state's two determinants have both electrons in orbitals directed perpendicular to the C-Ne axis. Because Ne is a closed-shell species, any electron density directed toward it will produce a "repulsive" antibonding interaction. As a result, we expect the $M_L = 1$ state to undergo a more repulsive interaction with the Ne atom than the $M_L = 0$ state.

Although one may be tempted to 'guess' how the various $^3P(M_L)$ states interact with a Ne atom by making an analogy between the three M_L states within the ^3P level and the three orbitals that comprise a set of p-orbitals, such analogies are not generally valid. The wavefunctions that correspond to term symbols are N-electron functions; they describe how N spin-orbitals are occupied and, therefore, how N spin-orbitals will be affected by interaction with an approaching 'ligand' such as a Ne atom. The net effect of the ligand will depend on the occupancy of all N spin-orbitals.

To illustrate this point, consider how the ^1S state of Carbon would be expected to interact with an approaching Ne atom. This term symbol's wavefunction $^1S = 3^{-1/2} [|p_0 \ p_0 \ | - |p_{-1} \ p_1 \ | - |p_1 \ p_{-1} \ |]$ contains three determinants, each with a 1/3 probability factor. The first, $|p_0 \ p_0 \ |$, produces a repulsive interaction with the closed-shell Ne; the second and third, $|p_{-1} \ p_1 \ |$ and $|p_1 \ p_{-1} \ |$, produce attractive interactions because they allow the Carbon's vacant p_0 orbital to serve in a Lewis acid capacity and accept electron density from Ne. The net effect is likely to be an attractive interaction because of the equal weighting of these three determinants in the ^1S wavefunction. This result could not have been 'guessed' by making making analogy with how an s-orbital interacts with a Ne atom; the ^1S state and an s-orbital are distinctly different in this respect.

Chapter 11

One Must be Able to Evaluate the Matrix Elements Among Properly Symmetry Adapted N-Electron Configuration Functions for Any Operator, the Electronic Hamiltonian in Particular. The Slater-Condon Rules Provide this Capability

I. CSFs Are Used to Express the Full N-Electron Wavefunction

It has been demonstrated that a given electronic configuration can yield several space- and spin- adapted determinental wavefunctions; such functions are referred to as configuration state functions (CSFs). These CSF wavefunctions are not the exact eigenfunctions of the many-electron Hamiltonian, H; they are simply functions which possess the space, spin, and permutational symmetry of the exact eigenstates. As such, they comprise an acceptable set of functions to use in, for example, a linear variational treatment of the true states.

In such variational treatments of electronic structure, the N-electron wavefunction Ψ is expanded as a sum over all CSFs that possess the desired spatial and spin symmetry:

$$\Psi = \sum_J C_J \Phi_J.$$

Here, the Φ_J represent the CSFs that are of the correct symmetry, and the C_J are their expansion coefficients to be determined in the variational calculation. If the spin-orbitals used to form the determinants, that in turn form the CSFs $\{\Phi_J\}$, are orthonormal one-electron functions (i.e., $<\phi_k | \phi_j> = \delta_{k,j}$), then the CSFs can be shown to be orthonormal functions of N electrons

$$< \Phi_J | \Phi_K > = \delta_{J,K}.$$

In fact, the Slater determinants themselves also are orthonormal functions of N electrons whenever orthonormal spin-orbitals are used to form the determinants.

The above expansion of the full N-electron wavefunction is termed a "configuration-interaction" (CI) expansion. It is, in principle, a mathematically rigorous approach to expressing Ψ because the set of all determinants that can be formed from a complete set of spin-orbitals can be shown to be complete. In practice, one is limited to the number of orbitals that can be used and in the number of CSFs that can be included in the CI expansion. Nevertheless, the CI expansion method forms the basis of the most commonly used techniques in quantum chemistry.

In general, the optimal variational (or perturbative) wavefunction for any (i.e., the ground or excited) state will include contributions from spin-and space-symmetry adapted determinants derived from all possible configurations. For example, although the determinant with L =1, S = 1, M_L =1, M_s =1 arising from the $1s^2 2s^2 2p^2$ configuration may contribute strongly to the true ground electronic state of the Carbon atom, there will be contributions from all configurations which can provide these L, S, M_L, and M_s values (e.g., the $1s^2 2s^2 2p^1 3p^1$ and $2s^2 2p^4$ configurations will also contribute, although the $1s^2 2s^2 2p^1 3s^1$ and $1s^2 2s^1 2p^2 3p^1$ will not because the latter two configurations are odd under inversion symmetry whereas the state under study is even).

The mixing of CSFs from many configurations to produce an optimal description of the true electronic states is referred to as configuration interaction (CI). Strong CI (i.e., mixing of CSFs with large amplitudes appearing for more than one dominant CSF) can occur, for example, when two CSFs from different electronic configurations have nearly the same Hamiltonian expectation value. For example, the $1s^2 2s^2$ and $1s^2 2p^2$ ^1S configurations of Be and the analogous ns^2 and np^2 configurations of all alkaline earth atoms are close in energy because the ns-np orbital energy splitting is small for these elements; the ^{2} and ^{2} configurations of ethylene become equal in energy, and thus undergo strong CI mixing, as the CC bond is twisted by 90° in which case the and * orbitals become degenerate.

Within a variational treatment, the relative contributions of the spin-and space-symmetry adapted CSFs are determined by solving a secular problem for the eigenvalues (E_i) and eigenvectors ($\underline{C}_i$) of the matrix representation H of the full many-electron Hamiltonian **H** within this CSF basis:

$$\sum_L H_{K,L} C_{i,L} = E_i C_{i,K}.$$

The eigenvalue E_i gives the variational estimate for the energy of the ith state, and the entries in the corresponding eigenvector $C_{i,K}$ give the contribution of the Kth CSF to the ith wavefunction Ψ_i in the sense that

$$\Psi_i = \sum_K C_{i,K} \Phi_K,$$

where Φ_K is the Kth CSF.

II. The Slater-Condon Rules Give Expressions for the Operator Matrix Elements Among the CSFs

To form the $H_{K,L}$ matrix, one uses the so-called <u>Slater-Condon rules</u> which express all non-vanishing determinental matrix elements involving either one- or two- electron operators (one-electron operators are additive and appear as

$$F = \sum_i f(i);$$

two-electron operators are pairwise additive and appear as

$$G = \sum_{ij} g(i,j)).$$

Because the CSFs are simple linear combinations of determinants with coefficients determined by space and spin symmetry, the $H_{I,J}$ matrix in terms of determinants can be used to generate the $H_{K,L}$ matrix over CSFs.

The Slater-Condon rules give the matrix elements between two determinants

$$|> = |\phi_1 \phi_2 \phi_3 \cdots \phi_N|$$

and

$$|'> = |\phi'_1 \phi'_2 \phi'_3 \cdots \phi'_N|$$

for <u>any</u> quantum mechanical operator that is a sum of one- and two- electron operators (F + G). It expresses these matrix elements in terms of one-and two-electron integrals involving the spin-orbitals that appear in $|>$ and $|'>$ and the operators f and g.

As a first step in applying these rules, one must examine $|>$ and $|'>$ and determine by how many (if any) spin-orbitals $|>$ and $|'>$ differ. In so doing, one may have to reorder the spin-orbitals in one of the determinants to achieve maximal coincidence with those in the other determinant; it is essential to keep track of the number of permutations (N_p) that one makes in achieving maximal coincidence. The results of the Slater-Condon rules given below are then multiplied by $(-1)^{N_p}$ to obtain the matrix elements between the original $|>$ and $|'>$. The final result does not depend on whether one chooses to permute $|>$ or $|'>$.

Once maximal coincidence has been achieved, the Slater-Condon (SC) rules provide the following prescriptions for evaluating the matrix elements of any operator F + G containing a one-electron part $F = \sum_i f(i)$ and a two-electron part $G = \sum_{ij} g(i,j)$ (the Hamiltonian is, of course, a specific example of such an operator; the electric dipole

operator $\sum_i e\mathbf{r}_i$ and the electronic kinetic energy $-\hbar^2/2m_e \sum_i \nabla_i^2$ are examples of one-electron operators (for which one takes $g = 0$); the electron-electron coulomb interaction $\sum_{i>j} e^2/r_{ij}$ is a two-electron operator (for which one takes $f = 0$)):

The Slater-Condon Rules

(i) If $|\rangle$ and $|'\rangle$ are identical, then

$$\langle|F+G|\rangle = \sum_i \langle \phi_i|f|\phi_i\rangle + \sum_{i>j} [\langle \phi_i\phi_j|g|\phi_i\phi_j\rangle - \langle \phi_i\phi_j|g|\phi_j\phi_i\rangle],$$

where the sums over i and j run over all spin-orbitals in $|\rangle$;

(ii) If $|\rangle$ and $|'\rangle$ differ by a single spin-orbital mismatch ($\phi_p \quad \phi'_p$),

$$\langle|F+G|'\rangle = \langle \phi_p|f|\phi'_p\rangle + \sum_j [\langle \phi_p\phi_j|g|\phi'_p\phi_j\rangle - \langle \phi_p\phi_j|g|\phi_j\phi'_p\rangle],$$

where the sum over j runs over all spin-orbitals in $|\rangle$ except ϕ_p;

(iii) If $|\rangle$ and $|'\rangle$ differ by two spin-orbitals ($\phi_p \quad \phi'_p$ and $\phi_q \quad \phi'_q$),

$$\langle|F+G|'\rangle = \langle \phi_p\phi_q|g|\phi'_p\phi'_q\rangle - \langle \phi_p\phi_q|g|\phi'_q\phi'_p\rangle$$

(note that the F contribution vanishes in this case);

(iv) If $|\rangle$ and $|'\rangle$ differ by three or more spin orbitals, then

$$\langle|F+G|'\rangle = 0;$$

(v) For the identity operator I, the matrix elements $\langle|I|'\rangle = 0$ if $|\rangle$ and $|'\rangle$ differ by one or more spin-orbitals (i.e., the Slater determinants are orthonormal if their spin-orbitals are).

Recall that each of these results is subject to multiplication by a factor of $(-1)^{N_p}$ to account for possible ordering differences in the spin-orbitals in $|\rangle$ and $|'\rangle$.

In these expressions,

$$\langle \phi_i|f|\phi_j\rangle$$

is used to denote the one-electron integral

$$\int \phi^*_i(r)\, f(r)\, \phi_j(r)\, dr$$

and

$$\langle \phi_i\phi_j|g|\phi_k\phi_l\rangle \text{ (or in short hand notation } \langle i\,j|k\,l\rangle)$$

represents the two-electron integral

$$\phi^*_i(r)\,\phi^*_j(r')\,g(r,r')\,\phi_k(r)\,\phi_l(r')\,drdr'.$$

The notation $<i\,j\,|\,k\,l>$ introduced above gives the two-electron integrals for the $g(r,r')$ operator in the so-called Dirac notation, in which the i and k indices label the spin-orbitals that refer to the coordinates r and the j and l indices label the spin-orbitals referring to coordinates r'. The r and r' denote r, θ, ϕ, and r', θ', ϕ' (with σ and σ' being the α or β spin functions). The fact that r and r' are integrated and hence represent 'dummy' variables introduces index permutational symmetry into this list of integrals. For example,

$$<i\,j\,|\,k\,l> = <j\,i\,|\,l\,k> = <k\,l\,|\,i\,j>^* = <l\,k\,|\,j\,i>^*;$$

the final two equivalences are results of the Hermitian nature of $g(r,r')$.

It is also common to represent these same two-electron integrals in a notation referred to as Mulliken notation in which:

$$\phi^*_i(r)\,\phi^*_j(r')\,g(r,r')\,\phi_k(r)\,\phi_l(r')\,drdr' = (i\,k\,|\,j\,l).$$

Here, the indices i and k, which label the spin-orbital having variables r are grouped together, and j and l, which label spin-orbitals referring to the r' variables appear together. The above permutational symmetries, when expressed in terms of the Mulliken integral list read:

$$(i\,k\,|\,j\,l) = (j\,l\,|\,i\,k) = (k\,i\,|\,l\,j)^* = (l\,j\,|\,k\,i)^*.$$

If the operators f and g do not contain any electron spin operators, then the spin integrations implicit in these integrals (all of the ϕ_i are spin-orbitals, so each ϕ is accompanied by an α or β spin function and each ϕ^* involves the adjoint of one of the α or β spin functions) can be carried out as $<\alpha|\alpha> =1, <\alpha|\beta> =0, <\beta|\alpha> =0, <\beta|\beta> =1$, thereby yielding integrals over spatial orbitals. These spin integration results follow immediately from the general properties of angular momentum eigenfunctions detailed in Appendix G; in particular, because α and β are eigenfunctions of S_z with different eigenvalues, they must be orthogonal $<\alpha|\beta> = <\beta|\alpha> = 0$.

The essential results of the Slater-Condon rules are:

1. The full N! terms that arise in the N-electron Slater determinants do not have to be treated explicitly, nor do the N!(N! + 1)/2 Hamiltonian matrix elements among the N! terms of one Slater determinant and the N! terms of the same or another Slater determinant.

2. All such matrix elements, for <u>any</u> one- and/or two-electron operator can be expressed in terms of one- or two-electron integrals over the spin-orbitals that appear in the determinants.

3. The integrals over orbitals are three or six dimensional integrals, regardless of how many electrons N there are.

4. These integrals over mo's can, through the LCAO-MO expansion, ultimately be expressed in terms of one- and two-electron integrals over the primitive atomic orbitals. It is only these ao-based integrals that can be evaluated explicitly (on high speed computers for all but the smallest systems).

III. Examples of Applying the Slater-Condon Rules

It is wise to gain some experience using the SC rules, so let us consider a few illustrative example problems.

1. What is the contribution to the total energy of the ^3P level of Carbon made by the two 2p orbitals alone? Of course, the two 1s and two 2s spin-orbitals contribute to the total energy, but we artificially ignore all such contributions in this example to simplify the problem.

Because all nine of the ^3P states have the same energy, we can calculate the energy of any one of them; it is therefore prudent to choose an "easy" one
$$^3P(M_L=1, M_S=1) = |p_1 \quad p_0 \quad |.$$
The energy of this state is $< |p_1 \quad p_0 \quad | H |p_1 \quad p_0 \quad | >$. The SC rules tell us this equals:

$$I_{2p_1} + I_{2p_0} + <2p_12p_0| 2p_12p_0> - <2p_12p_0| 2p_02p_1>,$$

where the short hand notation $I_j = <j| f |j>$ is introduced.

If the contributions from the two 1s and two 2s spin-orbitals are now taken into account, one obtains a <u>total</u> energy that also contains $2I_{1s} + 2I_{2s} + <1s1s|1s1s> + 4<1s2s|1s2s> - 2 <1s2s|2s1s> + <2s2s|2s2s> + 2<1s2p_1|1s2p_1> - <1s2p_1|2p_11s> + 2<1s2p_0|1s2p_0> - <1s2p_0|2p_01s> + 2<2s2p_1|2s2p_1> - <2s2p_1|2p_12s> + 2<2s2p_0|2s2p_0> - <2s2p_0|2p_02s>.$

2. Is the energy of another ^3P state equal to the above state's energy? Of course, but it may prove informative to prove this.

Consider the $M_S=0$, $M_L=1$ state whose energy is:

$$2^{-1/2}<[|p_1 \quad p_0 \quad | + |p_1 \quad p_0 \quad |]| H |<[|p_1 \quad p_0 \quad | + |p_1 \quad p_0 \quad |]>2^{-1/2}$$

$$=1/2\{I_{2p_1} + I_{2p_0} + <2p_12p_0| 2p_12p_0> + I_{2p_1} + I_{2p_0} + <2p_12p_0| 2p_12p_0>\}$$

$$+ 1/2 \{ - <2p_12p_0|2p_02p_1> - <2p_12p_0|2p_02p_1>\}$$

$$= I_{2p_1} + I_{2p_0} + <2p_12p_0| 2p_12p_0> - <2p_12p_0| 2p_02p_1>.$$

Which is, indeed, the same as the other ^3P energy obtained above.

3. What energy would the singlet state $2^{-1/2}<[|p_1 \quad p_0 \quad | - |p_1 \quad p_0 \quad |]$ have?

The ^3P $M_S=0$ example can be used (changing the sign on the two determinants) to give

$$E = I_{2p_1} + I_{2p_0} + <2p_12p_0| 2p_12p_0> + <2p_12p_0| 2p_02p_1>.$$

Note, this is the $M_L=1$ component of the ^1D state; it is, of course, not a ^1P state because no such state exists for two equivalent p electrons.

4. What is the CI matrix element coupling $|1s^22s^2|$ and $|1s^23s^2|$?

These two determinants differ by two spin-orbitals, so

$$<|1s \quad 1s \quad 2s \quad 2s \quad | H |1s \quad 1s \quad 3s \quad 3s \quad |> = <2s2s|3s3s> = <2s3s|3s2s>$$

(note, this is an exchange-type integral).

5. What is the CI matrix element coupling $|\qquad|$ and $|\qquad|$?

These two determinants differ by two spin-orbitals, so

$<\ |\ \ \ |H|\ \ \ \ \ |> = <\ \ |\ \ \ > = <\ \ *|\ *\ >$

(note, again this is an exchange-type integral).

6. What is the Hamiltonian matrix element coupling $|\ \ \ \ |$ and
$2^{-1/2}\ [\ |\ \ \ \ *\ |-|\ \ \ \ *\ |]$?

    The first determinant differs from the $\ ^2$ determinant by one spin-orbital, as does
the second (after it is placed into maximal coincidence by making one permutation), so

$<\ |\ \ \ \ |\ H|\ 2^{-1/2}\ [\ |\ \ \ \ *\ |-|\ \ \ \ *\ |]>$

$= 2^{-1/2}[<\ |f|\ \ *> + <\ \ |\ *\ >]\ -(-1)\ 2^{-1/2}[<\ |f|\ \ *> + <\ \ |\ *\ >]$

$= 2^{1/2}\ [<\ |f|\ \ *> + <\ \ |\ *\ >].$

7. What is the element coupling $|\ \ \ \ |$ and $2^{-1/2}\ [\ |\ \ \ \ *\ |+|\ \ \ \ *\ |]$?

$<\ |\ \ \ \ |\ H|\ 2^{-1/2}\ [\ |\ \ \ \ *\ |+|\ \ \ \ *\ |]>$

$= 2^{-1/2}[<\ |f|\ \ *> + <\ \ |\ *\ >]\ +(-1)\ 2^{-1/2}[<\ |f|\ \ *> + <\ \ |\ *\ >] = 0.$

This result should not surprise you because $|\ \ \ \ |$ is an S=0 singlet state while $2^{-1/2}\ [\ |\ \ \ \ *\ |+|\ \ \ \ *\ |]$ is the $M_S=0$ component of the S=1 triplet state.

8. What is the $\mathbf{r} = \sum_j e\mathbf{r}_j$ electric dipole matrix element between $|p_1\ p_1\ |$ and $2^{-1/2}[|p_1\ p_0\ | + |p_0\ p_1\ |]$? Is the second function a singlet or triplet? It is a singlet in disguise; by interchanging the p_0 and p_1 and thus introducing a (-1), this function is clearly identified as $2^{-1/2}[|p_1\ p_0\ | - |p_1\ p_0\ |]$ which is a singlet.

    The first determinant differs from the latter two by one spin orbital in each case, so

$<|p_1\ p_1\ |\mathbf{r}|2^{-1/2}[|p_1\ p_0\ | + |p_0\ p_1\ |]> =$

$2^{-1/2}[<p_1|\mathbf{r}|p_0> + <p_1|\mathbf{r}|p_0>] = 2^{1/2}\ <p_1|\mathbf{r}|p_0>.$

9. What is the electric dipole matrix elements between the $^1\Delta = |\phi_1\alpha\ \phi_1\beta\ |$ state and the $^1\Sigma = 2^{-1/2}[|\phi_1\alpha\ \phi_{-1}\beta\ | + |\phi_{-1}\alpha\ \phi_1\beta\ |]$ state?

$< 2^{-1/2}[|\phi_1\alpha\ \phi_{-1}\beta\ | + |\phi_{-1}\alpha\ \phi_1\beta\ |]\ |\mathbf{r}|\ \phi_1\alpha\ \phi_1\beta\ |>$

$= 2^{-1/2}[< \phi_{-1}|\mathbf{r}|\ \phi_1> + < \phi_{-1}|\mathbf{r}|\ \phi_1>]$

$= 2^{1/2} < \phi_{-1}|\mathbf{r}|\ \phi_1>.$

10. As another example of the use of the SC rules, consider the configuration interaction which occurs between the $1s^2 2s^2$ and $1s^2 2p^2$ ^{1}S CSFs in the Be atom.

The CSFs corresponding to these two configurations are as follows:

$\Phi_1 = |1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ |$

and

$\Phi_2 = 1/\sqrt{3}\ [\ |1s\alpha\ 1s\beta\ 2p_0\alpha\ 2p_0\beta\ | - |1s\alpha\ 1s\beta\ 2p_1\alpha\ 2p_{-1}\beta\ |$

$- |1s\alpha\ 1s\beta\ 2p_{-1}\alpha\ 2p_1\beta\ |\ ].$

The determinental Hamiltonian matrix elements needed to evaluate the 2x2 $H_{K,L}$ matrix appropriate to these two CSFs are evaluated via the SC rules. The first such matrix element is:

$< |1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ |\ H\ |1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ |>$

$= 2h_{1s} + 2h_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s}\ ,$

where

$h_i = < \phi_i\ |\ -\hbar^2/2m_e\ \nabla^2 - 4e^2/r\ |\ \phi_i>\ ,$

$J_{i,j} = < \phi_i\ \phi_j\ |\ e^2/r_{12}\ |\ \phi_i\ \phi_j>\ ,$

and

$$K_{ij} = \langle \phi_i \phi_j | e^2/r_{12} | \phi_j \phi_i \rangle$$

are the orbital-level <u>one-electron, coulomb, and exchange integrals</u>, respectively.

Coulomb integrals J_{ij} describe the coulombic interaction of one charge density (ϕ_i^2 above) with another charge density (ϕ_j^2 above); exchange integrals K_{ij} describe the interaction of an <u>overlap</u> charge density (i.e., a density of the form $\phi_i \phi_j$) with itself ($\phi_i \phi_j$ with $\phi_i \phi_j$ in the above).

The spin functions α and β which accompany each orbital in $|1s \, 1s \, 2s \, 2s|$ have been eliminated by carrying out the spin integrations as discussed above. Because H contains no spin operators, this is straightforward and amounts to keeping integrals $\langle \phi_i | f | \phi_j \rangle$ only if ϕ_i and ϕ_j are of the same spin and integrals $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ only if ϕ_i and ϕ_k are of the same spin <u>and</u> ϕ_j and ϕ_l are of the same spin. The physical content of the above energy (i.e., Hamiltonian expectation value) of the $|1s \, 1s \, 2s \, 2s|$ determinant is clear: $2h_{1s} + 2h_{2s}$ is the sum of the expectation values of the one-electron (i.e., kinetic energy and electron-nuclear coulomb interaction) part of the Hamiltonian for the four occupied spin-orbitals; $J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s}$ contains the coulombic repulsions among all pairs of occupied spin-orbitals minus the exchange interactions among pairs of spin-orbitals with like spin.

The determinental matrix elements linking Ψ_1 and Ψ_2 are as follows:

$$\langle |1s \, 1s \, 2s \, 2s| \, H \, |1s \, 1s \, 2p_0 \, 2p_0| \rangle = \langle 2s2s | 2p_02p_0 \rangle,$$

$$\langle |1s \, 1s \, 2s \, 2s| \, H \, |1s \, 1s \, 2p_1 \, 2p_{-1}| \rangle = \langle 2s2s | 2p_12p_{-1} \rangle,$$

$$\langle |1s \, 1s \, 2s \, 2s| \, H \, |1s \, 1s \, 2p_{-1} \, 2p_1| \rangle = \langle 2s2s | 2p_{-1}2p_1 \rangle,$$

where the Dirac convention has been introduced as a shorthand notation for the two-electron integrals (e.g., $\langle 2s2s | 2p_02p_0 \rangle$ represents $\int 2s^*(r_1)2s^*(r_2) \, e^2/r_{12} \, 2p_0(r_1) \, 2p_0(r_2) \, dr_1 \, dr_2$).

The three integrals shown above can be seen to be equal and to be of the exchange-integral form by expressing the integrals in terms of integrals over cartesian functions and recognizing identities due to the equivalence of the $2p_x$, $2p_y$, and $2p_z$ orbitals. For example,

$$\langle 2s2s | 2p_12p_{-1} \rangle = (1/\sqrt{2})^2 \{ \langle 2s \, 2s | [2p_x + i \, 2p_y] [2p_x - i \, 2p_y] \rangle \} =$$

$1/2 \{< 2s\ 2s\ |\ x\ x > + < 2s\ 2s\ |\ y\ y > +i < 2s\ 2s\ |\ y\ x > -i < 2s\ 2s\ |\ x\ y >\} =$

$< 2s\ 2s\ |\ x\ x > = K_{2s,x}$

(here the two imaginary terms cancel and the two remaining real integrals are equal);

$< 2s\ 2s\ 2p_0\ 2p_0 > = < 2s\ 2s\ |\ z\ z > = < 2s\ 2s\ |\ x\ x > = K_{2s,x}$

(this is because $K_{2s,z} = K_{2s,x} = K_{2s,y}$);

$< 2s\ 2s\ |\ 2p_{-1}2p_1 > = 1/2 \{< 2s\ 2s\ |\ [2p_x\ -i\ 2p_y]\ [2p_x\ +i\ 2p_y] >\} =$

$< 2s\ 2s\ |\ x\ x > = \quad 2s^*(r_1)\ 2s^*(r_2)\ e^2/r_{12}\ 2p_x(r_1)\ 2p_x(r_2)\ dr_1\ dr_2 = K_{2s,x}.$

These integrals are clearly of the exchange type because they involve the coulombic interaction of the 2s $2p_{x,y,or\ z}$ overlap charge density with itself.

      Moving on, the matrix elements among the three determinants in $\quad_2$ are given as follows:

$< |1s\ \ 1s\ \ 2p_0\ \ 2p_0\ \ |\ H\ |1s\ \ 1s\ \ 2p_0\ \ 2p_0\ \ | >$

$= 2h_{1s} + 2h_{2p} + J_{1s,1s} + J_{2pz,2pz} + 4J_{1s,2p} - 2K_{1s,2p}$

($J_{1s,2p}$ and $K_{1s,2p}$ are independent of whether the 2p orbital is $2p_x$, $2p_y$, or $2p_z$);

$< |1s\ \ 1s\ \ 2p_1\ \ 2p_{-1}\ \ |\ H\ |1s\ \ 1s\ \ 2p_1\ \ 2p_{-1}\ \ | >$

$= 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + <2p_12p_{-1}|2p_12p_{-1}>;$

$< |1s\ \ 1s\ \ 2p_{-1}\ \ 2p_1\ \ |\ H\ |1s\ \ 1s\ \ 2p_{-1}\ \ 2p_1\ \ | >$
$2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + <2p_{-1}2p_1|2p_{-1}2p_1>;$

$< |1s\ \ 1s\ \ 2p_0\ \ 2p_0\ \ |\ H\ |1s\ \ 1s\ \ 2p_1\ \ 2p_{-1}\ \ | > = < 2p_02p_0\ |\ 2p_12p_{-1} >$

$< |1s \ 1s \ 2p_0 \ 2p_0 \ | H | 1s \ 1s \ 2p_{-1} \ 2p_1 \ | > = < 2p_0 2p_0 | 2p_{-1} 2p_1 >$

$< |1s \ 1s \ 2p_1 \ 2p_{-1} \ | H | 1s \ 1s \ 2p_{-1} \ 2p_1 \ | > = < 2p_1 2p_{-1} | 2p_{-1} 2p_1 >.$

Certain of these integrals can be recast in terms of cartesian integrals for which equivalences are easier to identify as follows:

$< 2p_0 2p_0 | 2p_1 2p_{-1} > = < 2p_0 2p_0 | 2p_{-1} 2p_1 > = < z \ z | x \ x > = K_{z,x};$

$< 2p_1 2p_{-1} | 2p_{-1} 2p_1 > = < x \ x | y \ y > + 1/2[< x \ x | x \ x > - < x \ y | x \ y >]$

$= K_{x,y} + 1/2 [J_{x,x} - J_{x,y}];$

$< 2p_1 2p_{-1} | 2p_1 2p_{-1} > = < 2p_{-1} 2p_1 | 2p_{-1} 2p_1 > = 1/2(J_{x,x} + J_{x,y}).$

Finally, the 2x2 CI matrix corresponding to the CSFs Φ_1 and Φ_2 can be formed from the above determinental matrix elements; this results in:

$H_{11} = 2h_{1s} + 2h_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s} ;$

$H_{12} = -K_{2s,x} / \sqrt{3} ;$

$H_{22} = 2h_{1s} + 2h_{2p} + J_{1s,1s} + 4J_{1s,2p} - 2K_{1s,2p} + J_{z,z} - 2/3 \ K_{z,x}.$

The lowest eigenvalue of this matrix provides this CI calculation's estimate of the ground-state ^1S energy of Be; its eigenvector provides the CI amplitudes for Φ_1 and Φ_2 in this ground-state wavefunction. The other root of the 2x2 secular problem gives an approximation to another ^1S state of higher energy, in particular, a state dominated by the $3^{-1/2} [|1s \ 1s \ 2p_0 \ 2p_0 \ | - |1s \ 1s \ 2p_1 \ 2p_{-1} \ | - |1s \ 1s \ 2p_{-1} \ 2p_1 \ |]$ CSF.

11. As another example, consider the matrix elements which arise in electric dipole transitions between two singlet electronic states:
$< \Psi_1 | \mathbf{E} \cdot \sum_i e\mathbf{r}_i | \Psi_2 >$. Here $\mathbf{E} \cdot \sum_i e\mathbf{r}_i$ is the one-electron operator describing the interaction of an electric field of magnitude and polarization $\mathbf{E}$ with the instantaneous dipole moment

of the electrons (the contribution to the dipole operator arising from the nuclear charges $-\sum_a Z_a e^2 \mathbf{R}_a$ does not contribute because, when placed between Ψ_1 and Ψ_2, this zero-electron operator yields a vanishing integral because Ψ_1 and Ψ_2 are orthogonal).

When the states Ψ_1 and Ψ_2 are described as linear combinations of CSFs as introduced earlier ($\Psi_i = \sum_K C_{iK} \Phi_K$), these matrix elements can be expressed in terms of CSF-based matrix elements $< \Phi_K | \sum_i e \mathbf{r}_i | \Phi_L >$. The fact that the electric dipole operator is a one-electron operator, in combination with the SC rules, guarantees that only states for which the dominant determinants differ by at most a single spin-orbital (i.e., those which are "singly excited") can be connected via electric dipole transitions through first order (i.e., in a one-photon transition to which the $< \Psi_1 | \sum_i e \mathbf{r}_i | \Psi_2 >$ matrix elements pertain). It is for this reason that light with energy adequate to ionize or excite deep core electrons in atoms or molecules usually causes such ionization or excitation rather than double ionization or excitation of valence-level electrons; the latter are two-electron events.

In, for example, the $\pi => \pi^*$ excitation of an olefin, the ground and excited states are dominated by CSFs of the form (where all but the "active" π and π^* orbitals are not explicitly written) :

$$\Psi_1 = | ... \pi\alpha\pi\beta |$$

and

$$\Psi_2 = 1/\sqrt{2}[| ... \pi\alpha\pi^*\beta | - | ... \pi\beta\pi^*\alpha |].$$

The electric dipole matrix element between these two CSFs can be found, using the SC rules, to be

$$e/\sqrt{2} [< \pi |\mathbf{r}| \pi^* > + < \pi |\mathbf{r}| \pi^* >] = \sqrt{2} e < \pi |\mathbf{r}| \pi^* > .$$

Notice that in evaluating the second determinental integral
$< | ... \pi\beta\pi^*\alpha | e\mathbf{r} | ... \pi\alpha\pi^*\beta | >$, a sign change occurs when one puts the two determinants into maximum coincidence; this sign change then makes the minus sign in Ψ_2 yield a positive sign in the final result.

IV. Summary

In all of the above examples, the SC rules were used to reduce matrix elements of one- or two- electron operators between determinental functions to one- or two- electron integrals over the orbitals which appear in the determinants. In any <u>ab initio</u> electronic structure computer program there must exist the capability to form symmetry-adapted CSFs and to evaluate, using these SC rules, the Hamiltonian and other operators' matrix elements among these CSFs in terms of integrals over the mos that appear in the CSFs. The SC rules provide not only the tools to compute quantitative matrix elements; they allow one to understand in qualitative terms the strengths of interactions among CSFs. In the following section, the SC rules are used to explain why chemical reactions in which the reactants and products have dominant CSFs that differ by two spin-orbital occupancies often display activation energies that exceed the reaction endoergicity.

Chapter 12

Along "reaction paths", configurations can be connected one-to-one according to their symmetries and energies. This is another part of the Woodward-Hoffmann rules

I. Concepts of Configuration and State Energies

A. Plots of CSF Energies Give Configuration Correlation Diagrams

The energy of a particular electronic state of an atom or molecule has been expressed in terms of Hamiltonian matrix elements, using the SC rules, over the various spin-and spatially-
adapted determinants or CSFs which enter into the state wavefunction.

$$E = \sum_{I,J} < \Phi_I | H | \Phi_J > C_I C_J \, .$$

The diagonal matrix elements of H in the CSF basis multiplied by the appropriate CI amplitudes $< \Phi_I | H | \Phi_I > C_I C_I$ represent the energy of the Ith CSF weighted by the strength (C_I^2) of that CSF in the wavefunction. The off-diagonal elements represent the effects of mixing among the CSFs; mixing is strongest whenever two or more CSFs have nearly the same energy (i.e., $< \Phi_I | H | \Phi_I > \approx < \Phi_J | H | \Phi_J >$)
and there is strong coupling (i.e., $< \Phi_I | H | \Phi_J >$ is large). Whenever the CSFs are widely separated in energy, each wavefunction is dominated by a single CSF.

B. CSFs Interact and Couple to Produce States and State Correlation Diagrams

Just as orbital energies connected according to their symmetries and plotted as functions of geometry constitute an orbital correlation diagram, plots of the <u>diagonal CSF energies</u>, connected according to symmetry, constitute a <u>configuration correlation diagram</u> (CCD). If, near regions where energies of CSFs of the same symmetry cross (according to the direct product rule of group theory discussed in Appendix E, only CSFs of the same symmetry mix because only they have non-vanishing $< \Phi_I | H | \Phi_J >$ matrix elements), CI mixing is allowed to couple the CSFs to give rise to "avoided crossings", then the CCD is converted into a so-called <u>state correlation diagram</u> (SCD).

C. CSFs that Differ by Two Spin-Orbitals Interact Less Strongly than CSFs that Differ by One Spin-Orbital

The strengths of the couplings between pairs of CSFs whose energies cross are evaluated through the SC rules. CSFs that differ by more than two spin-orbital occupancies do not couple; the SC rules give vanishing Hamiltonian matrix elements for such pairs. Pairs that differ by two spin-orbitals (e.g. $|.. \phi_a... \phi_b...|$ vs $|.. \phi_{a'}... \phi_{b'}...|$) have interaction strengths determined by the two-electron integrals

$< ab \mid a'b' > - < ab \mid b'a'>$. Pairs that differ by a single spin-orbital (e.g. $|.. \; _a... ...|$ vs $|.. \; _{a'}... ...|$) are coupled by the one- and two- electron parts of H: $< a \mid f \mid b> + \; _j [< aj \mid bj> - < aj \mid jb >]$. Usually, couplings among CSFs that differ by two spin-orbitals are much weaker than those among CSFs that differ by one spin-orbital. In the latter case, the full strength of H is brought to bear, whereas in the former, only the electron-electron coulomb potential is operative.

D. State Correlation Diagrams

      In the SCD, the energies are connected by symmetry but the configurational nature as reflected in the C_I coefficients changes as one passes through geometries where crossings in the CCD occur. The SCD is the ultimate product of an orbital and configuration symmetry and energy analysis and gives one the most useful information about whether reactions will or will not encounter barriers on the ground and excited state surfaces.

      As an example of the application of CCD's and SCD's, consider the disrotatory closing of 1,3-butadiene to produce cyclobutene. The OCD given earlier for this proposed reaction path is reproduced below.
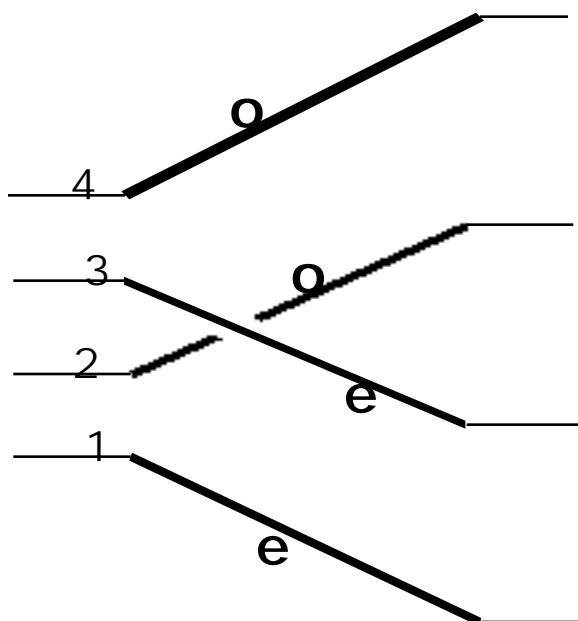
Recall that the symmetry labels e and o refer to the symmetries of the orbitals under reflection through the one C_v plane that is <u>preserved</u> throughout the proposed disrotatory

closing. Low-energy configurations (assuming one is interested in the thermal or low-lying photochemically excited-state reactivity of this system) for the reactant molecule and their overall space and spin symmetry are as follows:

(i) $\pi_1^2\,\pi_2^2 = 1e^2 1o^2$, ^{1}Even

(ii) $\pi_1^2\,\pi_2^1\,\pi_3^1 = 1e^2 1o^1 2e^1$, ^{3}Odd and ^{1}Odd.

For the product molecule, on the other hand, the low-lying states are

(iii) $\sigma^2\,\pi^2 = 1e^2 2e^2$, ^{1}Even

(iv) $\sigma^2\,\pi^1\,\pi^{*1} = 1e^2 2e^1 1o^1$, ^{3}Odd , ^{1}Odd.

Notice that although the lowest energy configuration at the reactant geometry $\pi_1^2\,\pi_2^2 = 1e^2 1o^2$ and the lowest energy configuration at the product geometry $\sigma^2\,\pi^2 = 1e^2 2e^2$ are both of ^{1}Even symmetry, they are <u>not</u> the same configurations; they involve occupancy of different symmetry orbitals.
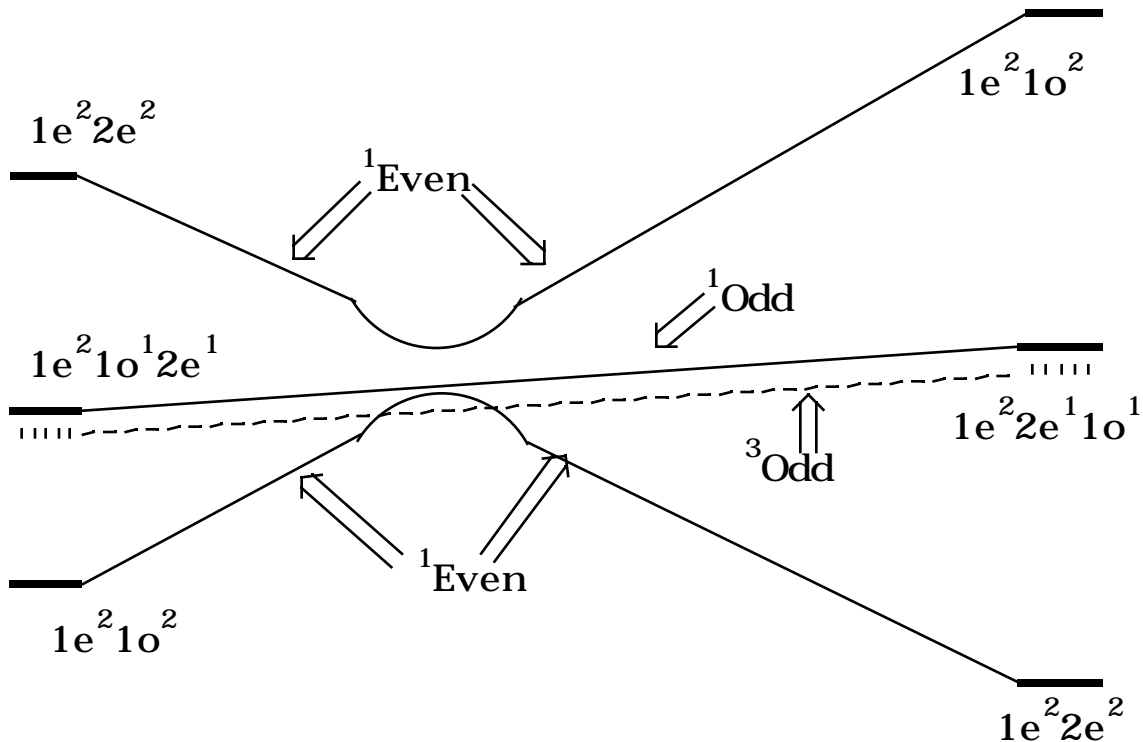
In constructing the CCD, one must trace the energies of all four of the above CSFs (actually there are more because the singlet and triplet excited CSFs must be treated independently) along the proposed reaction path. In doing so, one must realize that the $1e^2 1o^2$ CSF has low energy on the reactant side of the CCD because it corresponds to $\pi_1^2\,\pi_2^2$ orbital occupancy, but on the product side, it corresponds to $\sigma^2\,\pi^{*2}$ orbital occupancy and is thus of very high energy. Likewise, the $1e^2 2e^2$ CSF has low energy on the product side where it is $\sigma^2\,\pi^2$ but high energy on the reactant side where it corresponds to $\pi_1^2\,\pi_3^2$. The low-lying singly excited CSFs are $1e^2 2e^1 1o^1$ at both reactant and product geometries; in the former case, they correspond to $\pi_1^2\,\pi_2^1\,\pi_3^1$ occupancy and at the latter to $\sigma^2\,\pi^1\,\pi^{*1}$ occupancy. Plotting the energies of these CSFs along the disrotatory reaction path

results in the CCD shown below.
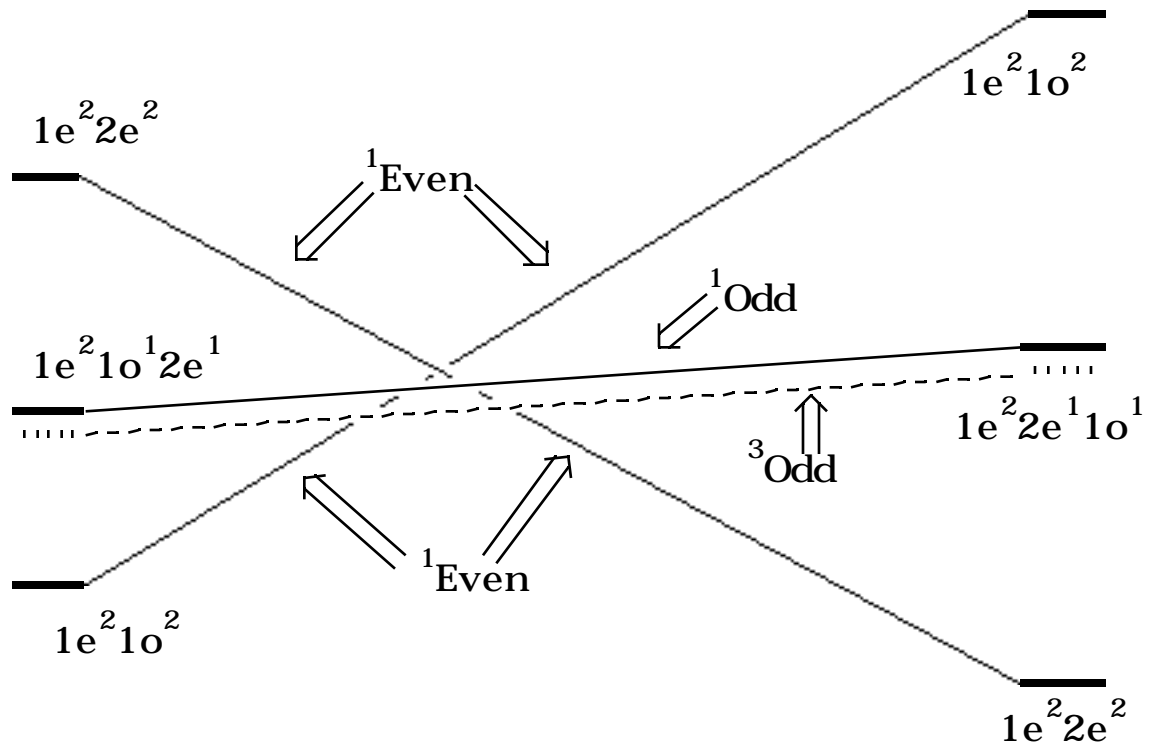
If the two [1]Even CSFs which cross are allowed to interact (the SC rules give their interaction strength in terms of the exchange integral
$< |1e^21o^2 | H | |1e^22e^2 | > = < 1o1o | 2e2e > = K_{1o,2e}$) to produce states which are combinations of the two [1]Even CSFs, the following SCD results:

$1e^2 1o^2$

$1e^2 2e^2$

^{1}Even

^{1}Odd

$1e^2 1o^1 2e^1$

^{3}Odd

$1e^2 2e^1 1o^1$

^{1}Even

$1e^2 1o^2$

$1e^2 2e^2$

       This SCD predicts that the thermal (i.e., on the ground electronic surface) disrotatory rearrangement of 1,3-butadiene to produce cyclobutene will experience a <u>symmety-imposed barrier</u> which arises because of the avoided crossing of the two ^{1}Even configurations; this avoidance occurs because the orbital occupancy pattern (i.e., the configuration) which is best for the ground state of the reactant is not identical to that of the product molecule. The SCD also predicts that there should be no symmetry-imposed barrier for the singlet or triplet excited-state rearrangement, although the reaction leading from excited 1,3-butadiene to excited cyclobutene may be endothermic on the grounds of bond strengths alone.

       It is also possible to infer from the SCD that excitation of the lowest singlet state of 1,3-butadiene would involve a low quantum yield for producing cyclobutene and would, in fact, produce ground-state butadiene. As the reaction proceeds along the singlet surface this ^{1}Odd state intersects the ground ^{1}Even surface on the <u>reactant side</u> of the diagram; internal conversion (i.e., quenching from the ^{1}Odd to the ^{1}Even surfaces induced by using a vibration of odd symmetry to "digest" the excess energy (much like vibronic borrowing in spectroscopy) can lead to production of ground-state reactant molecules. Some fraction of such events will lead to the system remaining on the ^{1}Odd surface until, further along the reaction path, the ^{1}Odd surface again intersects the ^{1}Even surface on the <u>product side</u> at which time quenching to produce ground-state products can occur.

Although, in principle, it is possible for some fraction of the events to follow the ^{1}Odd surface beyond this second intersection and to thus lead to ^{1}Odd product molecules that might fluoresce, quenching is known to be rapid in most polyatomic molecules; as a result, reactions which are chemiluminescent are rare. An appropriate introduction to the use of OCD's, CCD's, and SCD's as well as the radiationless processes that can occur in thermal and photochemical reactions is given in the text Energetic Principles of Chemical Reactions , J. Simons, Jones and Bartlett, Boston (1983).

II. Mixing of Covalent and Ionic Configurations

As chemists, much of our intuition concerning chemical bonds is built on simple models introduced in undergraduate chemistry courses. The detailed examination of the H_2 molecule via the valence bond and molecular orbital approaches forms the basis of our thinking about bonding when confronted with new systems. Let us examine this model system in further detail to explore the electronic states that arise by occupying two orbitals (derived from the two 1s orbitals on the two hydrogen atoms) with two electrons.

In total, there exist six electronic states for all such two-orbital, two-electron systems. The heterolytic fragments X + Y: and X: + Y produce two singlet states; the homolytic fragments X• + Y• produce one singlet state and a set of three triplet states having M_S = 1, 0, and -1. Understanding the relative energies of these six states , their bonding and antibonding characters, and which molecular state dissociates to which asymptote are important.

Before proceeding, it is important to clarify the notation (e.g., X•, Y•, X, Y: , etc.), which is designed to be applicable to neutral as well as charged species. In all cases considered here, only two electrons play active roles in the bond formation. These electrons are represented by the dots. The symbols X• and Y• are used to denote species in which a single electron is attached to the respective fragment. By X: , we mean that both electrons are attached to the X- fragment; Y means that neither electron resides on the Y- fragment. Let us now examine the various bonding situations that can occur; these examples will help illustrate and further clarify this notation.

A. The H_2 Case in Which Homolytic Bond Cleavage is Favored

To consider why the two-orbital two-electron single bond formation case can be more complex than often thought, let us consider the H_2 system in more detail. In the molecular orbital description of H_2, both bonding $_g$ and antibonding $_u$ mos appear.

There are two electrons that can both occupy the σ_g mo to yield the ground electronic state H$_2$($^1\Sigma_g^+$, σ_g^2); however, they can also occupy both orbitals to yield $^3\Sigma_u^+$($\sigma_g^1\sigma_u^1$) and $^1\Sigma_u^+$($\sigma_g^1\sigma_u^1$), or both can occupy the σ_u mo to give the $^1\Sigma_g^+$(σ_u^2) state. As demonstrated explicitly below, these latter two states dissociate heterolytically to X + Y **:** = H$^+$ + H$^-$, and are sufficiently high in energy relative to X• + Y• = H + H that we ordinarily can ignore them. However, their presence and character are important in the development of a full treatment of the molecular orbital model for H$_2$ and are <u>essential</u> to a proper treatment of cases in which heterolytic bond cleavage is favored.

B. Cases in Which Heterolytic Bond Cleavage is Favored

For some systems one or both of the heterolytic bond dissociation asymptotes (e.g., X+ Y **:** or X **:** + Y) may be <u>lower</u> in energy than the homolytic bond dissociation asymptote. Thus, the states that are analogues of the $^1\Sigma_u^+$($\sigma_g^1\sigma_u^1$) and $^1\Sigma_g^+$(σ_u^2) states of H$_2$ can no longer be ignored in understanding the valence states of the XY molecules. This situation arises quite naturally in systems involving transition metals, where interactions between empty metal or metal ion orbitals and 2-electron donor ligands are ubiquitous.

Two classes of systems illustrate cases for which heterolytic bond dissociation lies lower than the homolytic products. The first involves transition metal dimer cations, M$_2^+$. Especially for metals to the right side of the periodic table, such cations can be considered to have ground-state electron configurations with ^{2}d^{n}d^{n+1} character, where the d electrons are not heavily involved in the bonding and the σ bond is formed primarily from the metal atom s orbitals. If the σ bond is homolytically broken, one forms X• + Y• = M (s^{1}d^{n+1}) + M$^+$ (s^{1}d^n). For most metals, this dissociation asymptote lies higher in energy than the heterolytic products X **:** + Y = M (s^{2}d^n) + M$^+$ (s^{0}d^{n+1}), since the latter electron configurations correspond to the ground states for the neutrals and ions, respectively. A prototypical species which fits this bonding picture is Ni$_2^+$.

The second type of system in which heterolytic cleavage is favored arises with a metal-ligand complex having an atomic metal ion (with a s^{0}d^{n+1} configuration) and a two electron donor, L **:** . A prototype is (Ag C$_6$H$_6$)$^+$ which was observed to photodissociate to form X• + Y• = Ag(^{2}S, s^{1}d^{10}) + C$_6$H$_6^+$(^{2}B$_1$) rather than the lower energy (heterolytically cleaved) dissociation limit Y + X **:** = Ag$^+$(^{1}S, s^{0}d^{10}) + C$_6$H$_6$ (^{1}A$_1$).

C. Analysis of Two-Electron, Two-Orbital, Single-Bond Formation

1. Orbitals, Configurations and States

The resultant family of six electronic states can be described in terms of the six configuration state functions (CSFs) that arise when one occupies the pair of bonding σ and antibonding σ* molecular orbitals with two electrons. The CSFs are combinations of Slater determinants formed to generate proper spin- and spatial symmetry- functions.

The spin- and spatial- symmetry adapted N-electron functions referred to as CSFs can be formed from one or more Slater determinants. For example, to describe the singlet CSF corresponding to the closed-shell σ² orbital occupancy, a single Slater determinant

$$^1\Sigma(0) = |\sigma\alpha \sigma\beta| = (2)^{-1/2}\{\sigma\alpha(1)\sigma\beta(2) - \sigma\beta(1)\sigma\alpha(2)\}$$

suffices. An analogous expression for the (σ*)² CSF is given by

$$^1\Sigma^{**}(0) = |\sigma^*\alpha \sigma^*\beta| = (2)^{-1/2}\{\sigma^*\alpha(1)\sigma^*\beta(2) - \sigma^*\beta(2)\sigma^*\alpha(1)\}.$$

Also, the $M_S = 1$ component of the triplet state having σσ* orbital occupancy can be written as a single Slater determinant:

$$^3\Sigma^*(1) = |\sigma\alpha \sigma^*\alpha| = (2)^{-1/2}\{\sigma\alpha(1)\sigma^*\alpha(2) - \sigma^*\alpha(1)\sigma\alpha(2)\},$$

as can the $M_S = -1$ component of the triplet state

$$^3\Sigma^*(-1) = |\sigma\beta \sigma^*\beta| = (2)^{-1/2}\{\sigma\beta(1)\sigma^*\beta(2) - \sigma^*\beta(1)\sigma\beta(2)\}.$$

However, to describe the singlet CSF and $M_S = 0$ triplet CSF belonging to the σσ* occupancy, two Slater determinants are needed:

$$^1\Sigma^*(0) = \frac{1}{\sqrt{2}}[\,|\sigma\alpha \sigma^*\beta| - |\sigma\beta \sigma^*\alpha|\,]$$

is the singlet CSF and

$$^3\Sigma^*(0) = \frac{1}{\sqrt{2}}[\,|\sigma\alpha \sigma^*\beta| + |\sigma\beta \sigma^*\alpha|\,]$$

is the triplet CSF. In each case, the spin quantum number S, its z-axis projection M_S , and the   quantum number are given in the conventional $2S+1$ (M_S) notation.

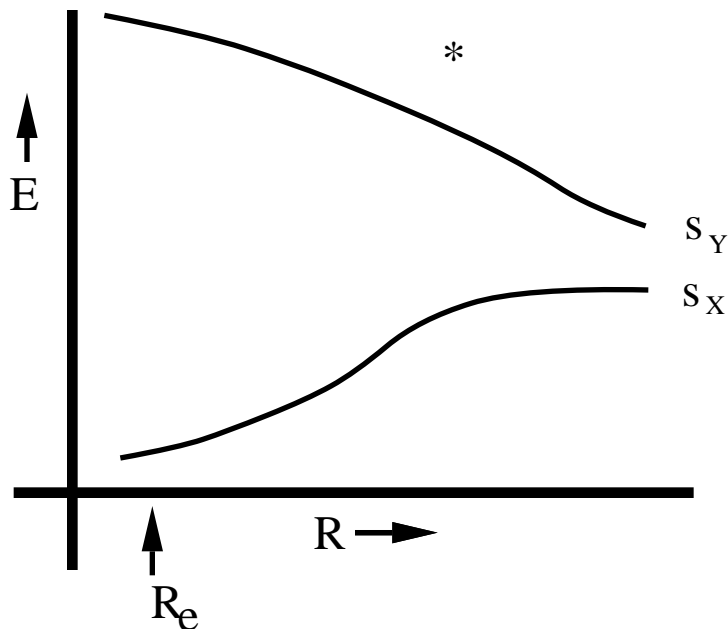## 2. Orbital, CSF, and State Correlation Diagrams

i. Orbital Diagrams

The two orbitals of the constituent atoms or functional groups (denoted s_x and s_y for convenience and in anticipation of considering groups X and Y that possess valence s orbitals) combine to form a bonding $=$ $_g$ molecular orbital and an antibonding $* =$ $_u$ molecular orbital (mo). As the distance R between the X and Y fragments is changed from near its equilibrium value of R_e and approaches infinity, the energies of the   and $*$ orbitals vary in a manner well known to chemists as depicted below.
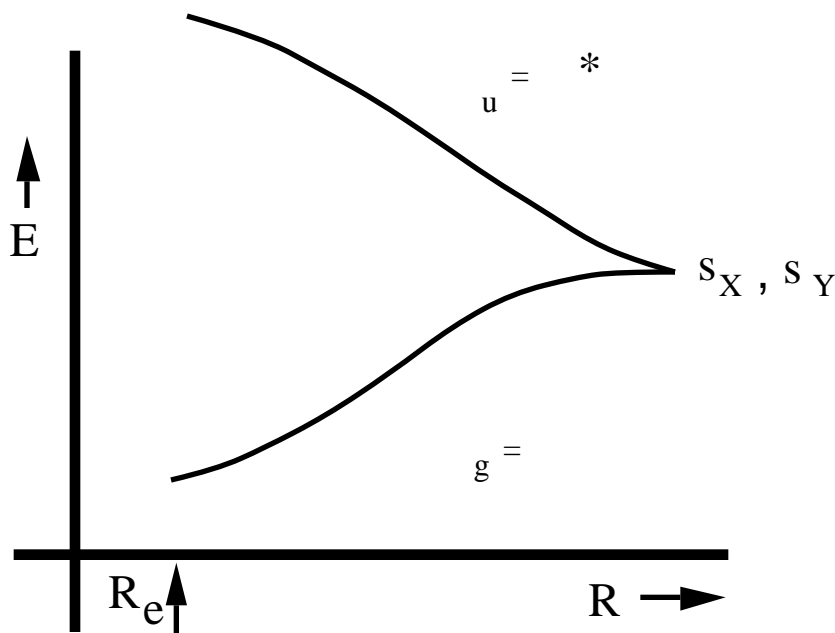
Energies of the bonding   and antibonding $*$ orbitals as functions of interfragment distance; R_e denotes a distance near the equilibrium bond length for XY.

In the heteronuclear case, the s_x and s_y orbitals still combine to form a bonding and an antibonding $*$ orbital, although these orbitals no longer belong to g and u symmetry. The energies of these orbitals, for R values ranging from near R_e to R   , are depicted below.

Energies of the bonding σ and antibonding σ* orbitals as functions of internuclear distance. Here, X is more electronegative than Y.

For the homonuclear case, as R approaches ∞, the energies of the σ_g and σ_u orbitals become degenerate. Moreover, as R → O, the orbital energies approach those of the united atom. In the heteronuclear situation, as R approaches ∞, the energy of the σ orbital approaches the energy of the s_x orbital, and the σ* orbital converges to the s_y orbital energy. Unlike the homonuclear case, the σ and σ* orbitals are <u>not</u> degenerate as R → ∞. The energy "gap" between the σ and σ* orbitals at R = ∞ depends on the electronegativity difference between the groups X and Y. If this gap is small, it is expected that the behavior of this (slightly) heteronuclear system should approach that of the homonuclear X_2 and Y_2 systems. Such similarities are demonstrated in the next section.

ii. Configuration and State Diagrams

The energy variation in these orbital energies gives rise to variations in the energies of the six CSFs and of the six electronic states that arise as combinations of these CSFs. The three singlet ($^1\Sigma$ (0), $^1\Sigma$* (0), and $^1\Sigma$** (0)) and three triplet ($^3\Sigma$*(1), $^3\Sigma$*(0) and $^3\Sigma$*(-1)) CSFs are, by no means, the true electronic eigenstates of the system; they are simply spin and spatial angular momentum adapted antisymmetric spin-orbital products. In principle, the set of CSFs Φ of the same symmetry must be combined to form the proper electronic eigenstates Ψ of the system:

$$= C \quad .$$

Within the approximation that the valence electronic states can be described adequately as combinations of the above valence CSFs, the three $^1\Sigma$, $^1\Sigma^*$, and $^1\Sigma^{**}$ CSFs must be combined to form the three lowest energy valence electronic states of $^1\Sigma$ symmetry. For the homonuclear case, the $^1\Sigma^*$ CSF does not couple with the other two because it is of ungerade symmetry, while the other CSFs $^1\Sigma$ and $^1\Sigma^{**}$ have gerade symmetry and do combine.

The relative amplitudes C of the CSFs within each state are determined by solving the configuration-interaction (CI) secular problem:

$$\sum_J H_{\ J} C_J = E \ C$$

for the state energies E and state CI coefficient vectors C. Here, H is the electronic Hamiltonian of the molecule.

To understand the extent to which the $^1\Sigma$ and $^1\Sigma^{**}$ (and $^1\Sigma^*$ for heteronuclear cases) CSFs couple, it is useful to examine the energies $H_{\ J}$ of these CSFs for the range of internuclear distances of interest $R_e < R < \infty$. Near R_e, where the energy of the σ orbital is substantially below that of the σ^* orbital, the $\sigma^{2} \ ^1\Sigma$ CSF lies significantly below the $\sigma\sigma^* \ ^1\Sigma^*$ CSF which, in turn lies below the σ^{*2} $^1\Sigma^{**}$ CSF; the large energy splittings among these three CSFs simply reflecting the large gap between the σ and σ^* orbitals. The $^3\Sigma^*$ CSF generally lies below the corresponding $^1\Sigma^*$ CSF by an amount related to the exchange energy between the σ and σ^* orbitals.

As $R \to \infty$, the CSF energies $H_{\ J}$ are more difficult to "intuit" because the σ and σ^* orbitals become degenerate (in the homonuclear case) or nearly so. To pursue this point and arrive at an energy ordering for the CSFs that is appropriate to the $R \to \infty$ region, it is useful to express each of the above CSFs in terms of the atomic orbitals s_x and s_y that comprise σ and σ^*. To do so, the LCAO-MO expressions for σ and σ^*,

$$\sigma = C \,[s_x + z \, s_y]$$

and

$$\sigma^* = C^* \,[z \, s_x - s_y],$$

are substituted into the Slater determinant definitions of the CSFs. Here C and C* are the normalization constants. The parameter z is 1.0 in the homonuclear case and deviates from 1.0 in relation to the s_x and s_y orbital energy difference (if s_x lies below s_y, then z < 1.0; if s_x lies above s_y, z > 1.0).

To simplify the analysis of the above CSFs, the familiar homonuclear case in which z = 1.0 will be examined first. The process of substituting the above expressions for   and   * into the Slater determinants that define the singlet and triplet CSFs can be illustrated as follows:

$$^1 \ (0) = \qquad = C^2 \ (s_x + s_y) \ (s_x + s_y)$$

$$= C^2 [\ s_x \quad s_x \quad + \quad s_y \quad s_y \quad + \quad s_x \quad s_y \quad + \quad s_y \quad s_x \quad]$$

The first two of these atomic-orbital-based Slater determinants ($s_x \quad s_x$ and $s_y \quad s_y$) are denoted "ionic" because they describe atomic orbital occupancies, which are appropriate to the R   region, that correspond to X: + Y and X + Y: valence bond structures, while $s_x \quad s_y$ and $s_y \quad s_x$ are called "covalent" because they correspond to X• + Y• structures.

In similar fashion, the remaining five CSFs may be expressed in terms of atomic-orbital-based Slater determinants. In so doing, use is made of the antisymmetry of the Slater determinants
$| \ _1 \ _2 \ _3 | = - | \ _1 \ _3 \ _2 |$, which implies that any determinant in which two or more spin-orbitals are identical vanishes $| \ _1 \ _2 \ _2 | = - | \ _1 \ _2 \ _2 | = 0$. The result of decomposing the mo-based CSFs into their atomic orbital components is as follows:

$$^1 \ {**} (0) = \quad * \quad *$$
$$= C^{*2} [\ s_x \quad s_x \quad + \quad s_y \quad s_y$$
$$- \ s_x \quad s_y \quad - \ s_y \quad s_x \quad]$$

$$^1 \ {*} (0) = \frac{1}{\sqrt{2}} [\qquad * \quad - \qquad * \quad]$$
$$= CC^* \sqrt{2} \ [\ s_x \quad s_x \quad - \ s_y \quad s_y \quad]$$

$$^3 \ {*} (1) = \qquad *$$
$$= CC^* \ 2 \ s_y \quad s_x$$

$$^3\Psi^*(0) = \frac{1}{\sqrt{2}}\,[\qquad * \quad + \qquad * \quad]$$

$$= CC^* \sqrt{2}\,[\;s_y \quad s_x \quad - \quad s_x \quad s_y\;]$$

$$^3\Psi^*(-1) = \qquad *$$

$$= CC^*\,2\;s_y \quad s_x$$

These decompositions of the six valence CSFs into atomic-orbital or valence bond components allow the R = energies of the CSFs to be specified. For example, the fact that both $^1\Psi$ and $^1\Psi^{**}$ contain 50% ionic and 50% covalent structures implies that, as R , both of their energies will approach the average of the covalent and ionic atomic energies 1/2 [E (X•) + E (Y•) + E (Y) + E (X:)]. The $^1\Psi^*$ CSF energy approaches the purely ionic value E (Y)+ E (X:) as R . The energies of $^3\Psi^*(0)$, $^3\Psi^*(1)$ and $^3\Psi^*(-1)$ all approach the purely covalent value E (X•) + E (Y•) as R .

The behaviors of the energies of the six valence CSFs as R varies are depicted below for situations in which the homolytic bond cleavage is energetically favored (i.e., for which E (X•) + E (Y•) < E (Y)+ E (X:)).
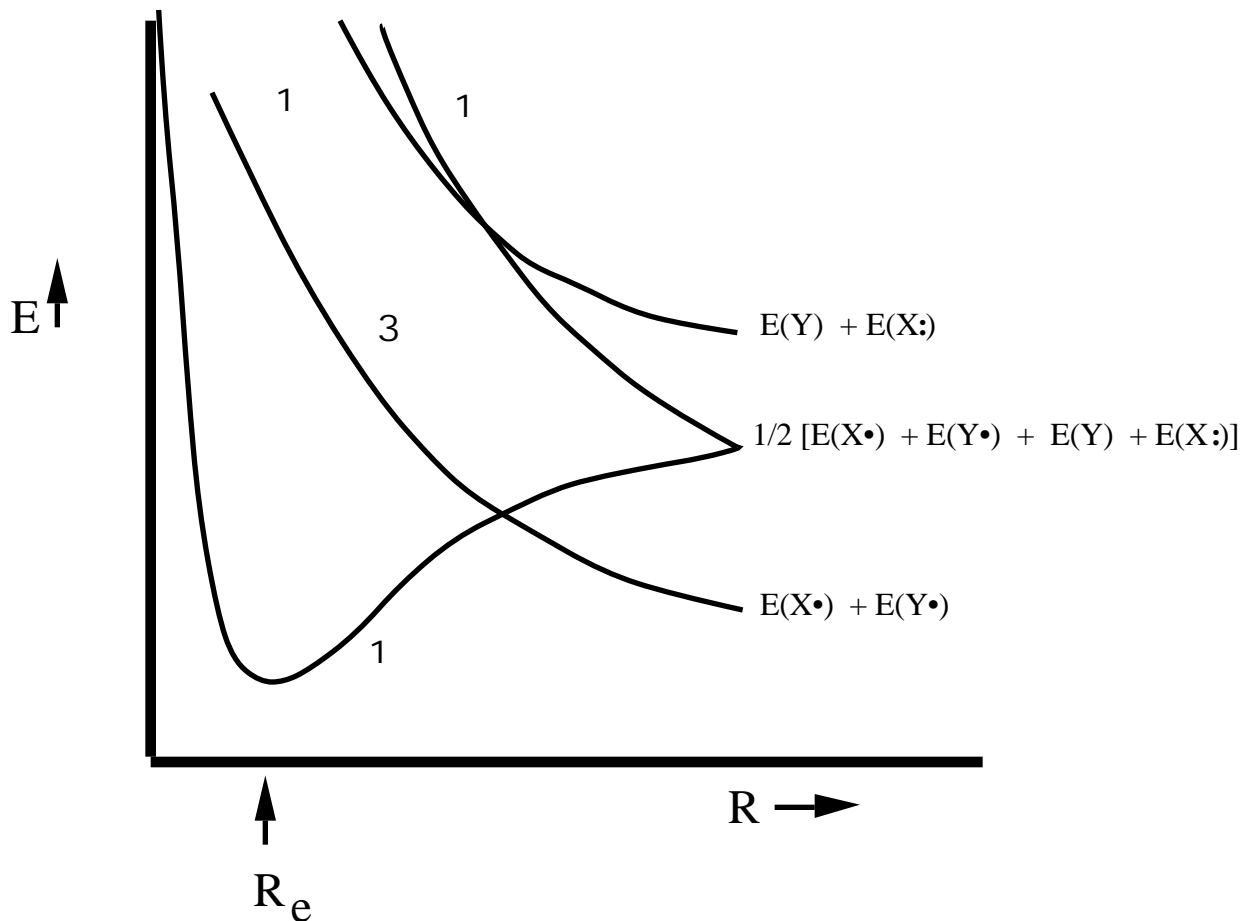
Configuration correlation diagram for homonuclear case in which homolytic bond cleavage is energetically favored.

When heterolytic bond cleavage is favored, the configuration energies as functions of internuclear distance vary as shown below.

E

$E(X\bullet) + E(Y\bullet)$

$1/2\ [E(X\bullet) + E(Y\bullet) + E(Y) + E(X\!:\!)]$

$E(Y) + E(X\!:\!)$

R →
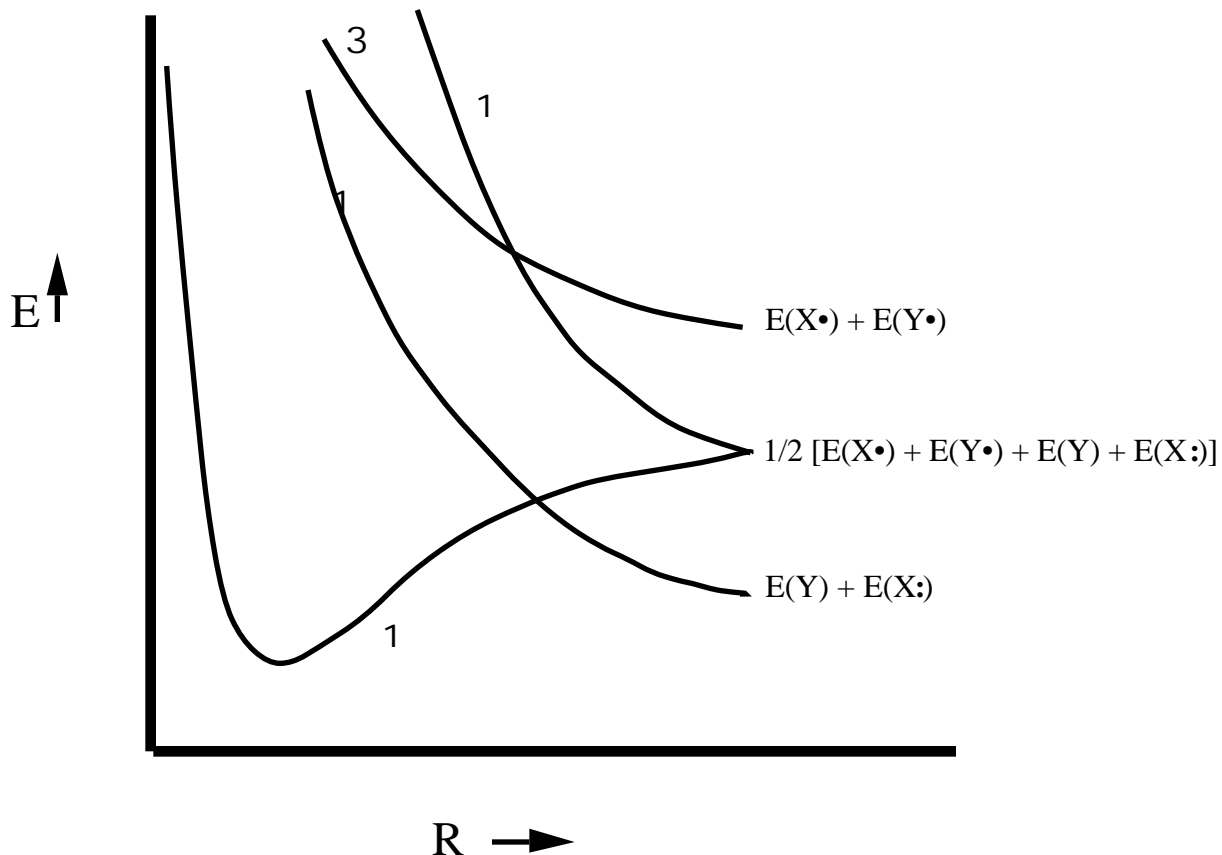
Configuration correlation diagram for a homonuclear case in which heterolytic bond cleavage is energetically favored.

It is essential to realize that the energies H of the CSFs do <u>not</u> represent the energies of the true electronic states E_K ; the CSFs are simply spin- and spatial-symmetry adapted antisymmetric functions that form a <u>basis</u> in terms of which to expand the true electronic states. For R-values at which the CSF energies are separated widely, the true E_K are rather well approximated by individual H values; such is the case near R_e.

For the homonuclear example, the ^{1} and ^{1} ** CSFs undergo CI coupling to form a pair of states of ^{1} symmetry (the ^{1} * CSF cannot partake in this CI mixing because it is of ungerade symmetry; the ^{3} * states can not mix because they are of triplet spin symmetry). The CI mixing of the ^{1} and ^{1} ** CSFs is described in terms of a 2x2 secular problem

$$\begin{vmatrix} \langle ^1\Sigma |H| ^1\Sigma\rangle & \langle ^1\Sigma |H| ^1\Sigma^{**}\rangle \\ \langle ^1\Sigma^{**}|H| ^1\Sigma\rangle & \langle ^1\Sigma^{**}| |^1\Sigma^{**}\rangle \end{vmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = E \begin{pmatrix} A \\ B \end{pmatrix}$$

The diagonal entries are the CSF energies depicted in the above two figures. Using the Slater-Condon rules, the off-diagonal coupling can be expressed in terms of an exchange integral between the σ and σ* orbitals:

$$\langle ^1\Sigma |H| ^1\Sigma^{**}\rangle = \langle \sigma\sigma |H| \sigma^*\sigma^*\rangle = \langle \sigma\sigma | \frac{1}{r_{12}} | \sigma^*\sigma^*\rangle = K_{\sigma\sigma^*}$$

At R → ∞, where the $^1\Sigma$ and $^1\Sigma^{**}$ CSFs are degenerate, the two solutions to the above CI secular problem are:

$$E_{\mp}^{\pm} = 1/2 \,[\, E(X\bullet) + E(Y\bullet) + E(Y{:}) + E(X{:}) \,] \mp_{+} \frac{1}{r_{12}} \langle \sigma^*\sigma^* \rangle$$

with respective amplitudes for the $^1\Sigma$ and $^1\Sigma^{**}$ CSFs given by

$$A_{-}^{+} = \pm \frac{1}{\sqrt{2}} ; \qquad B_{-}^{+} = \mp \frac{1}{\sqrt{2}} .$$

The first solution thus has

$$\Psi_{-} = \frac{1}{\sqrt{2}} [\, |\sigma\sigma| - |\sigma^*\sigma^*| \,]$$

which, when decomposed into atomic valence bond components, yields

$$\Psi_{-} = \frac{1}{\sqrt{2}} [\, |s_x s_y| - |s_x s_y| \,].$$

The other root has

$$\Psi_{+} = \frac{1}{\sqrt{2}} [\, |\sigma\sigma| + |\sigma^*\sigma^*| \,]$$
$$= \frac{1}{\sqrt{2}} [\, |s_x s_x| + |s_y s_y| \,].$$

Clearly, $^1\Sigma$ and $^1\Sigma^{**}$, which both contain 50% ionic and 50% covalent parts, combine to produce Ψ_{-} which is purely covalent and Ψ_{+} which is purely ionic.

The above strong CI mixing of $^1\Sigma$ and $^1\Sigma^{**}$ as R qualitatively alters the configuration correlation diagrams shown above. Descriptions of the resulting valence singlet and triplet <u>states</u> are given below for homonuclear situations in which covalent products lie below and above ionic products, respectively. Note that in both cases, there exists a single attractive curve and five (n.b., the triplet state has three curves superposed) repulsive curves.
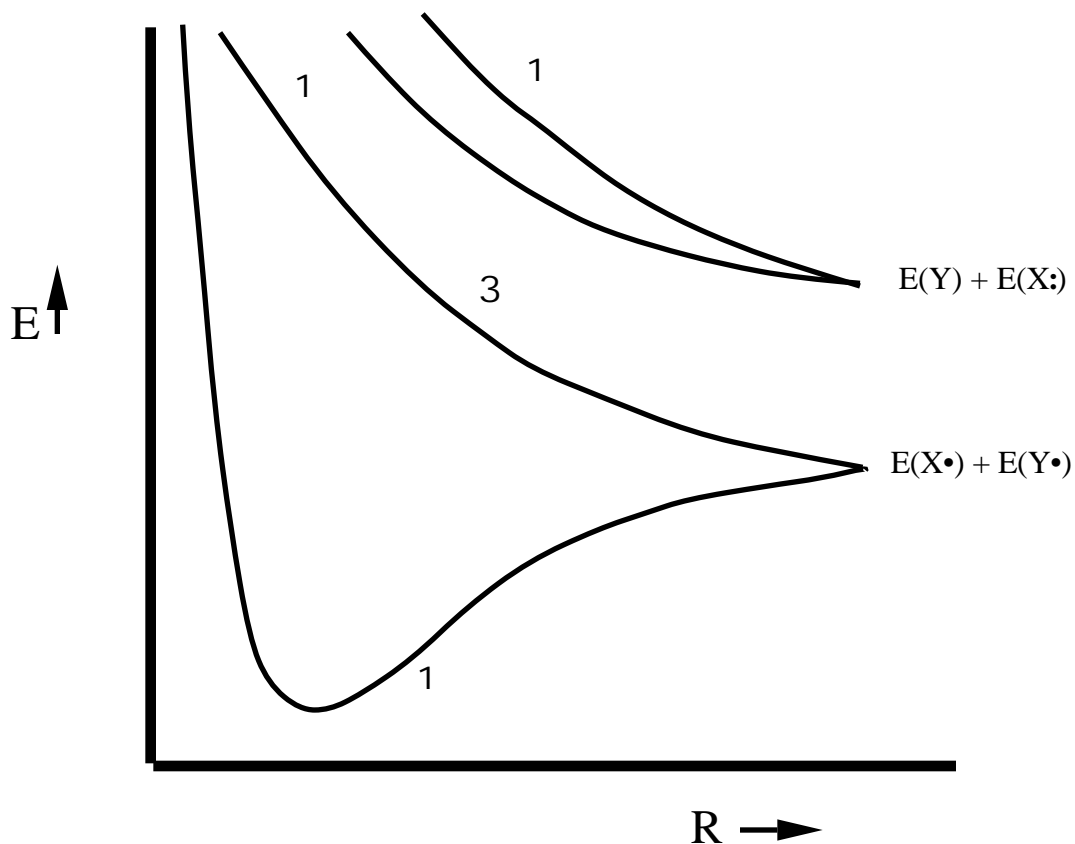
State correlation diagram for homonuclear case in which homolytic bond cleavage is energetically favored.
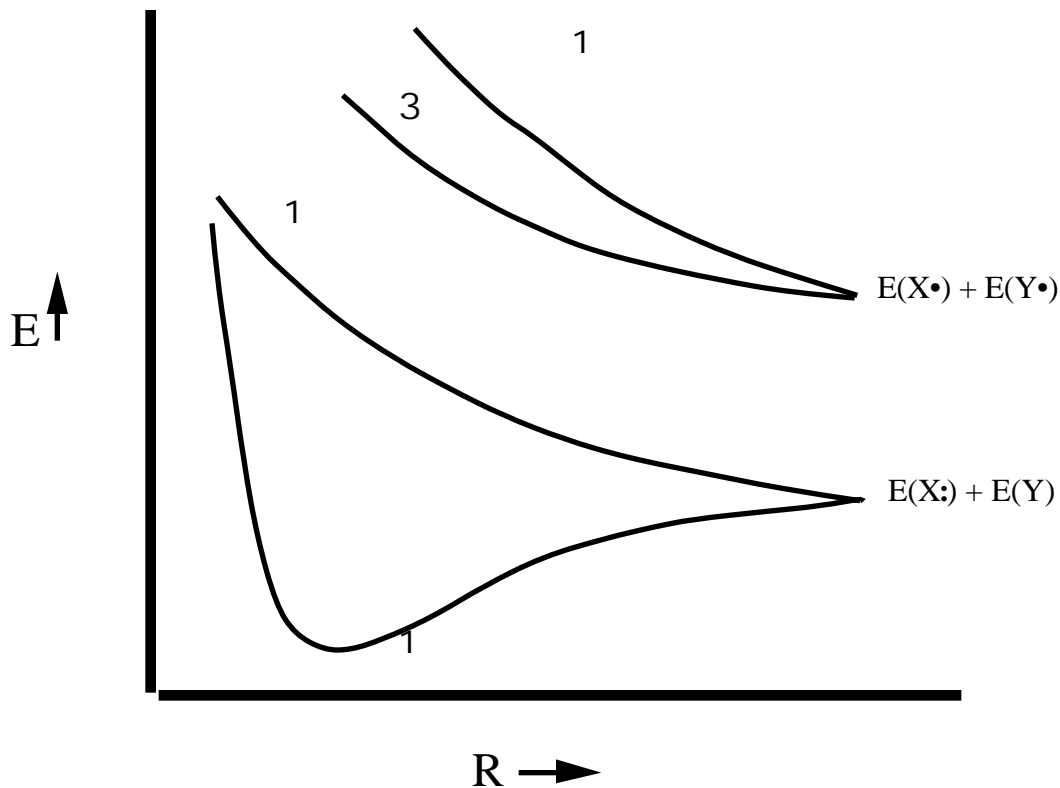
State correlation diagram for homonuclear case in which heterolytic bond cleavage is energetically favored.

If the energies of the s_x and s_y orbitals do not differ significantly (compared to the coulombic interactions between electron pairs), it is expected that the essence of the findings described above for homonuclear species will persist even for heteronuclear systems. A decomposition of the six CSFs listed above, using the heteronuclear molecular orbitals introduced earlier yields:

$$^1\Sigma(0) = C^2 [\ s_x\ s_x\ \ +z^2\ s_y\ s_y$$
$$+z\ s_x\ s_y\ \ +z\ s_y\ s_x\ \ ]$$

$$^1\Sigma^{**}(0) = C^{*2} [z^2\ s_x\ s_x\ \ +\ s_y\ s_y$$
$$-z\ s_x\ s_y\ \ -z\ s_y\ s_x\ ]$$

$$^1\Sigma^{*}(0) = \frac{CC^*}{\sqrt{2}} [\ 2z\ s_x\ s_x\ \ -2z\ s_y\ s_y$$
$$+ (\ z^2 - 1)\ s_y\ s_x\ \ + (z^2 - 1)\ s_x\ s_y\ \ ]$$

$$^3\Psi^*(0) = \frac{CC^*}{\sqrt{2}}\,(z^2 + 1)\,[\ s_y\ s_x\ -\ s_x\ s_y\ ]$$

$$^3\Psi^*(1) = CC^*\,(z^2 + 1)\ \ s_y\ s_x$$

$$^3\Psi^*(-1) = CC^*\,(z^2 + 1)\ \ s_y\ s_x$$

Clearly, the three $^3\Psi^*$ CSFs retain purely covalent R character even in the heteronuclear case. The $^1\Sigma$, $^1\Sigma^{**}$, and $^1\Sigma^*$ (all three of which can undergo CI mixing now) possess one covalent and two ionic components of the form $s_x\ s_y\ +\ s_y\ s_x$, $s_x\ s_x$, and $s_y\ s_y$. The three singlet CSFs therefore can be combined to produce a singlet covalent product function $s_x\ s_y\ +\ s_y\ s_x$ as well as <u>both</u> $X + Y$: and X : $+ Y$ ionic product wavefunctions $s_y\ s_y$ and $s_x\ s_x$, respectively. In most situations, the energy ordering of the homolytic and heterolytic dissociation products will be either $E(X\bullet) + E(Y\bullet) < E(X\text{:}) + E(Y) < E(X) + E(Y\text{:})$ or $E(X\text{:}) + E(Y) < E(X\bullet) + E(Y\bullet) < E(X) + E(Y\text{:})$.

The extensions of the state correlation diagrams given above to the heteronuclear situations are described below.
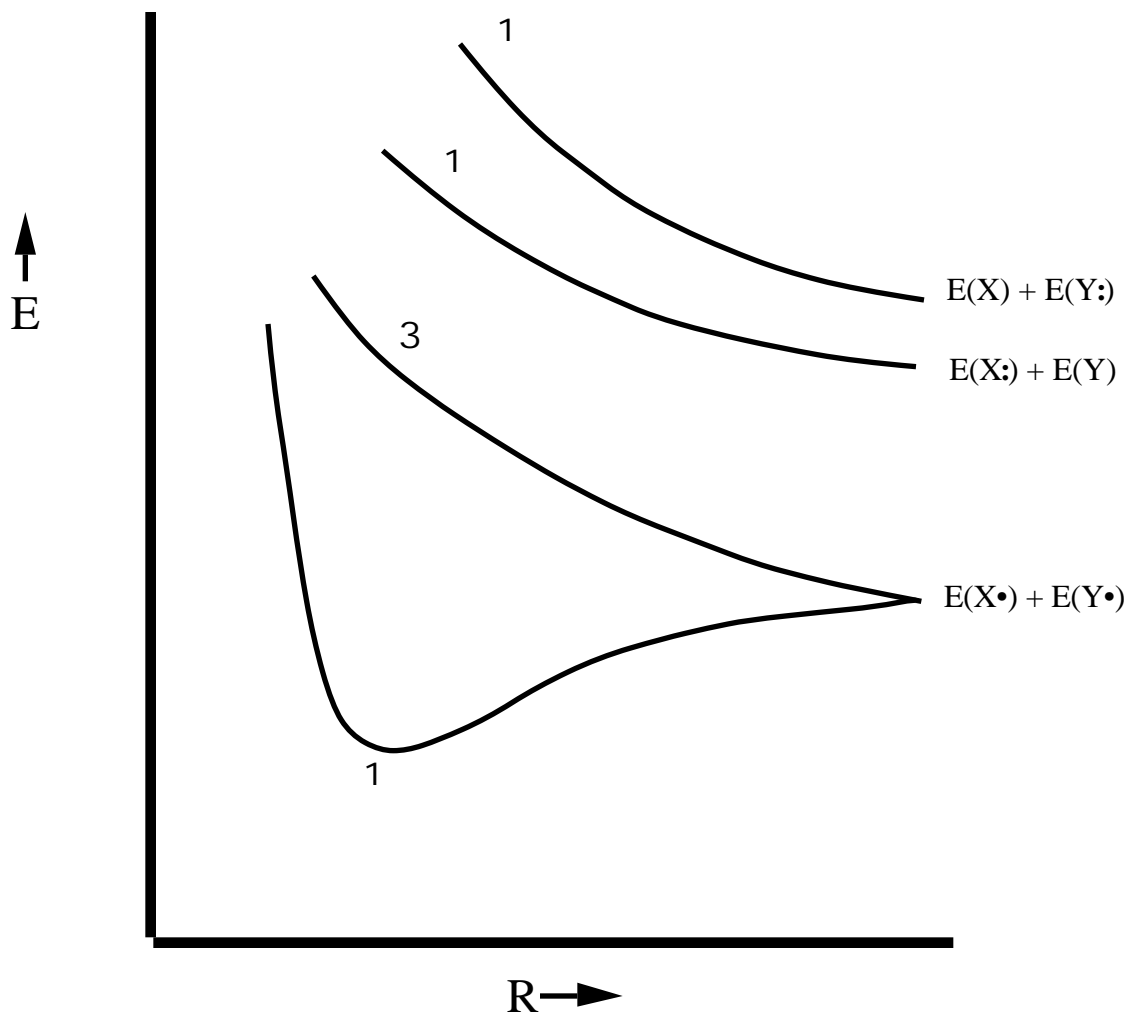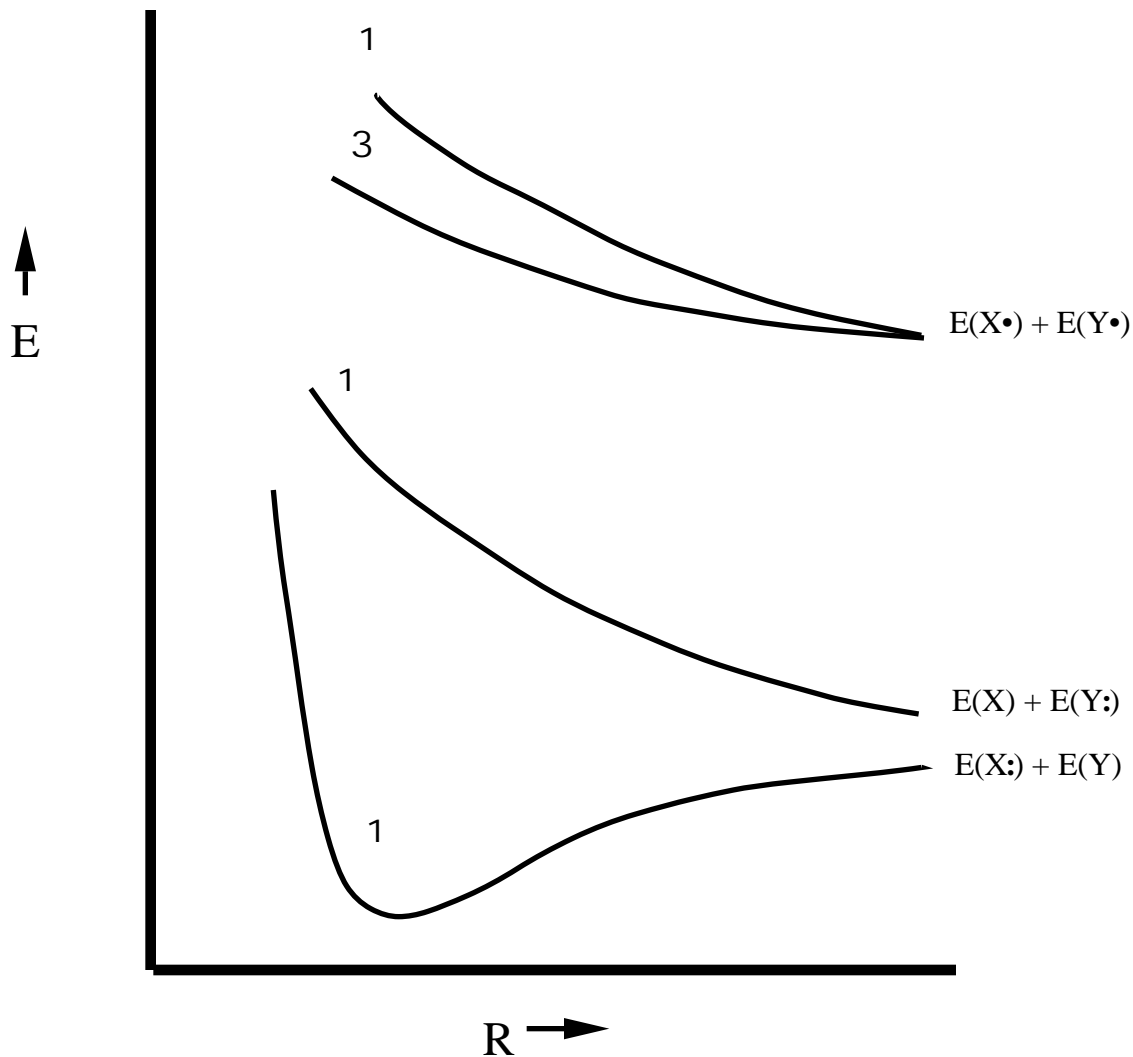
State correlation diagram for heteronuclear case in which homolytic bond cleavage is energetically favored.
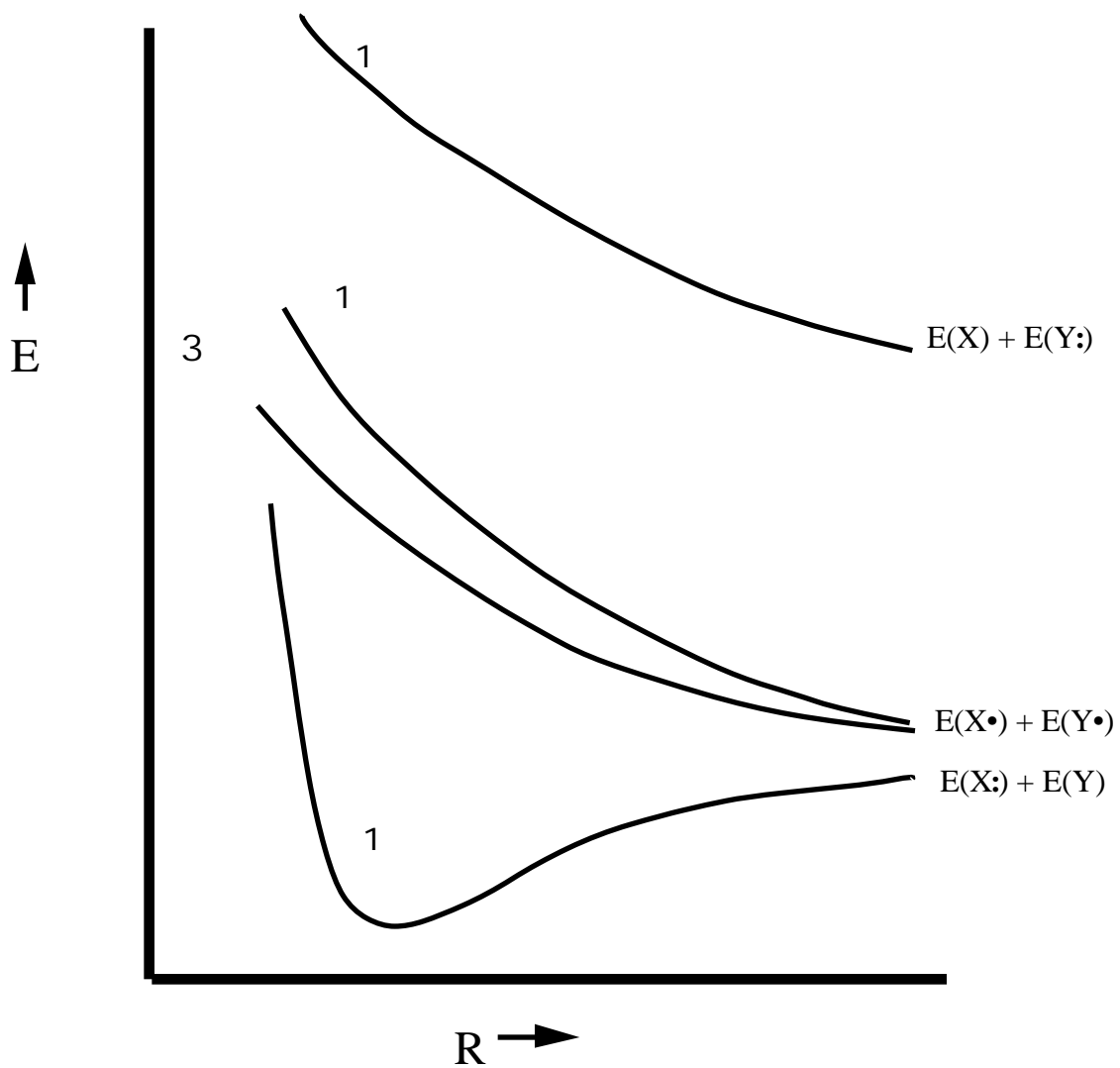
State correlation diagram for heteronuclear case in which heterolytic bond cleavage to one product is energetically favored but homolytic cleavage lies below the second heterolytic asymptote.

State correlation diagram for heteronuclear case in which both heterolytic bond cleavage products are energetically favored relative to homolytic cleavage.

Again note that only one curve is attractive and five are repulsive in all cases. In these heteronuclear cases, it is the mixing of the $^1\Sigma$, $^1\Sigma^*$, and $^1\Sigma^{**}$ CSFs, which varies with R, that determines which molecular state connects to which asymptote. As the energy ordering of the asymptotes varies, so do these correlations.

3. Summary

Even for the relatively simple two-electron, two-orbital single-bond interactions between a pair of atoms or functional groups, the correlations among energy-ordered molecular states and energy-ordered asymptotic states is complex enough to warrant considerations beyond what is taught in most undergraduate and beginning graduate inorganic and physical chemistry classes. In particular, the correlations that arise when one (or both) of the heterolytic bond dissociation aysmptotes lies below the homolytic cleavage products are important to realize and keep in mind.

In all cases treated here, the three singlet states that arise produce one and only one attractive (bonding) potential energy curve; the other two singlet surfaces are repulsive. The three triplet surfaces are also repulsive. Of course, in arriving at these conclusions, we have considered only contributions to the inter-fragment interactions that arise from valence-orbital couplings; no consideration has been made of attractive or repulsive forces that result from one or both of the X- and Y- fragments possessing net charge. In the latter case, one must, of course, add to the qualitative potential surfaces described here any coulombic, charge-dipole, or charge-induced-dipole energies. Such additional factors can lead to attractive long-range interactions in typical ion-molecule complexes.

The necessity of the analysis developed above becomes evident when considering dissociation of diatomic transition metal ions. Most transition metal atoms have ground states with electron configurations of the form $s^2 d^n$ (for first-row metals, exceptions include Cr ($s^1 d^5$), Cu ($s^1 d^{10}$), and the $s^1 d^9$ state of Ni is basically isoenergetic with the $s^2 d^8$ ground state). The corresponding positive ions have ground states with $s^1 d^n$ (Sc, Ti, Mn, Fe) or $s^0 d^{n+1}$ (V, Cr, Co, Ni, Cu) electron configurations . For each of these elements, the alternate electron configuration leads to low-lying excited states.

One can imagine forming a M_2^+ metal dimer ion with a configuration described as $\sigma_g^2 d^{2n+1}$, where the σ_g bonding orbital is formed primarily from the metal s orbitals and the d orbitals are largely nonbonding (as is particularly appropriate towards the right hand side of the periodic table). Cleavage of such a σ bond tends to occur heterolytically since this forms lower energy species, $M(s^2 d^n) + M^+(s^0 d^{n+1})$, than homolytic cleavage to $M(s^1 d^{n+1}) + M^+(s^1 d^n)$. For example, Co_2^+ dissociates to $Co(s^2 d^7) + Co^+(s^0 d^8)$ rather than to $Co(s^1 d^8) + Co^+(s^1 d^7)$,[2] which lies 0.85 eV higher in energy.

Qualitative aspects of the above analysis for homonuclear transition metal dimer ions will persist for heteronuclear ions. For example, the ground-state dissociation asymptote for CoNi$^+$ is the heterolytic cleavage products $Co(s^2 d^7) + Ni^+(s^0 d^9)$. The alternative heterolytic cleavage to form $Co^+(s^0 d^8) + Ni(s^2 d^8)$ is 0.23 eV higher in energy, while homolytic cleavage can lead to $Co^+(s^1 d^7) + Ni(s^1 d^9)$, 0.45 eV higher, or $Co(s^1 d^8) + Ni^+(s^1 d^8)$, 1.47 eV higher. This is the situation illustrated in the last figure above.

III. Various Types of Configuration Mixing

A. Essential CI

The above examples of the use of CCD's show that, as motion takes place along the proposed reaction path, geometries may be encountered at which it is essential to describe the electronic wavefunction in terms of a linear combination of more than one CSF:

$$\Psi = \sum_I C_I \Phi_I,$$

where the Φ_I are the CSFs which are undergoing the avoided crossing. Such essential configuration mixing is often referred to as treating "essential CI".

B. Dynamical CI

To achieve reasonable chemical accuracy (e.g., ± 5 kcal/mole) in electronic structure calculations it is necessary to use a multiconfigurational Ψ even in situations where no obvious strong configuration mixing (e.g., crossings of CSF energies) is present. For example, in describing the π^2 bonding electron pair of an olefin or the ns^2 electron pair in alkaline earth atoms, it is important to mix in doubly excited CSFs of the form $(\pi^*)^2$ and np^2, respectively. The reasons for introducing such a CI-level treatment were treated for an alkaline earth atom earlier in this chapter.

Briefly, the physical importance of such doubly-excited CSFs can be made clear by using the identity:

$$C_1 | ..\phi\alpha\phi\beta..| - C_2 | ..\phi'\alpha\phi'\beta..|$$

$$= C_1/2 \{ | ..(\phi - x \phi')\alpha (\phi + x \phi')\beta ..| - | ..(\phi - x \phi')\beta (\phi + x \phi')\alpha ..| \},$$

where

$$x = (C_2/C_1)^{1/2} .$$

This allows one to interpret the combination of two CSFs which differ from one another by a double excitation from one orbital (ϕ) to another (ϕ') as equivalent to a singlet coupling of

two different (non-orthogonal) orbitals (- x ') and (+ x '). This picture is closely related to the so-called generalized valence bond (GVB) model that W. A. Goddard and his co-workers have developed (see, for example, W. A. Goddard and L. B. Harding, Annu. Rev. Phys. Chem. <u>29</u>, 363 (1978)). In the simplest embodiment of the GVB model, each electron pair in the atom or molecule is correlated by mixing in a CSF in which that electron pair is "doubly excited" to a correlating orbital. The direct product of all such pair correlations generates the GVB-type wavefunction. In the GVB approach, these electron correlations are not specified in terms of double excitations involving CSFs formed from orthonormal spin orbitals; instead, explicitly non-orthogonal GVB orbitals are used as described above, but the result is the same as one would obtain using the direct product of doubly excited CSFs.

In the olefin example mentioned above, the two non-orthogonal "polarized orbital pairs" involve mixing the and * orbitals to produce two left-right polarized orbitals as depicted below:

$$ + \mathbf{x} \qquad\qquad -\mathbf{x} $$

left polarized   right polarized
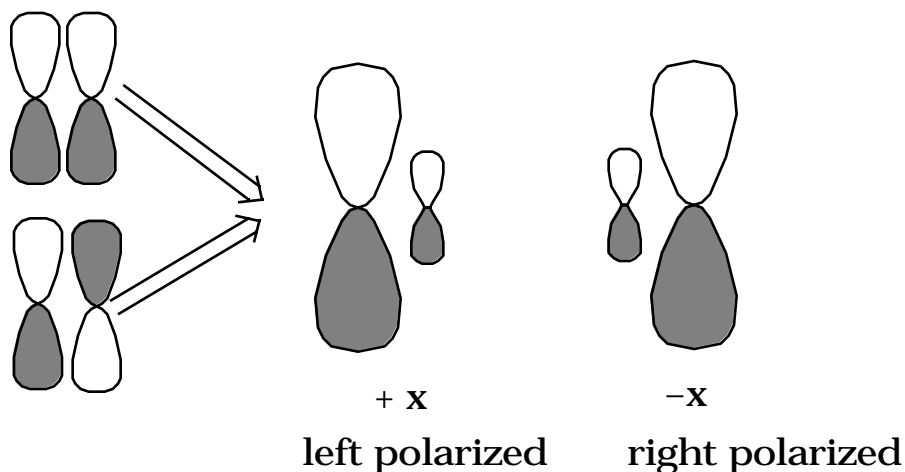
In this case, one says that the ^{2} electron pair undergoes left-right correlation when the (*)^2 CSF is mixed into the CI wavefunction.

In the alkaline earth atom case, the polarized orbital pairs are formed by mixing the ns and np orbitals (actually, one must mix in equal amounts of p_1, p_{-1} , and p_0 orbitals to preserve overall ^1S symmetry in this case), and give rise to angular correlation of the electron pair. Use of an (n+1)s^2 CSF for the alkaline earth calculation would contribute in-out or radial correlation because, in this case, the polarized orbital pair formed from the ns and (n+1)s orbitals would be radially polarized.

The use of doubly excited CSFs is thus seen as a mechanism by which can place electron <u>pairs</u>, which in the single-configuration picture occupy the same orbital, into

different regions of space (i.e., one into a member of the polarized orbital pair) thereby lowering their mutual coulombic repulsions. Such electron correlation effects are referred to as "dynamical electron correlation"; they are extremely important to include if one expects to achieve chemically meaningful accuracy (i.e., ± 5 kcal/mole).