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.

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

The diagonal matrix elements of H in the CSF basis multiplied by the appropriate CI amplitudes $< \Phi_I \mid H \mid \Phi_I > C_I C_I$ 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., $< \Phi_I \mid H \mid \Phi_I > \quad < \Phi_J \mid H \mid \Phi_J >$)
and there is strong coupling (i.e., $< \Phi_I \mid H \mid \Phi_J >$ 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 diagonal CSF energies, connected according to symmetry, constitute a configuration correlation diagram (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 $< \Phi_I \mid H \mid \Phi_J >$ 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 state correlation diagram (SCD).

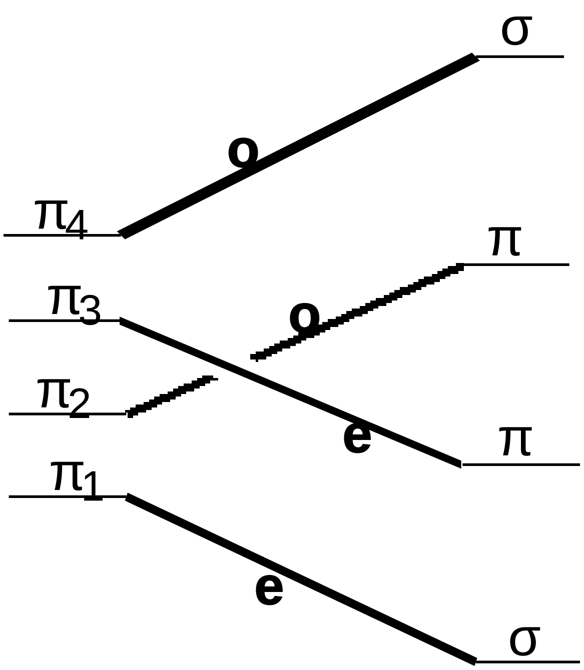
C. CSFs that Differ by Two Spin-Orbitals Interact Less Strongly than CSFs that Differ by One Spin-Orbital

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. $|..\ \varphi_a...\ \varphi_b...|$ vs $|..\ \varphi_{a'}...\ \varphi_{b'}...|$) 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. $|..\ \varphi_a...\ ...|$ vs $|..\ \varphi_{a'}...\ ...|$) are coupled by the one- and two- electron parts of H: $< a \mid f \mid b> + \Sigma_j [< aj \mid bj> - < aj \mid jb >]$. 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 preserved 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.

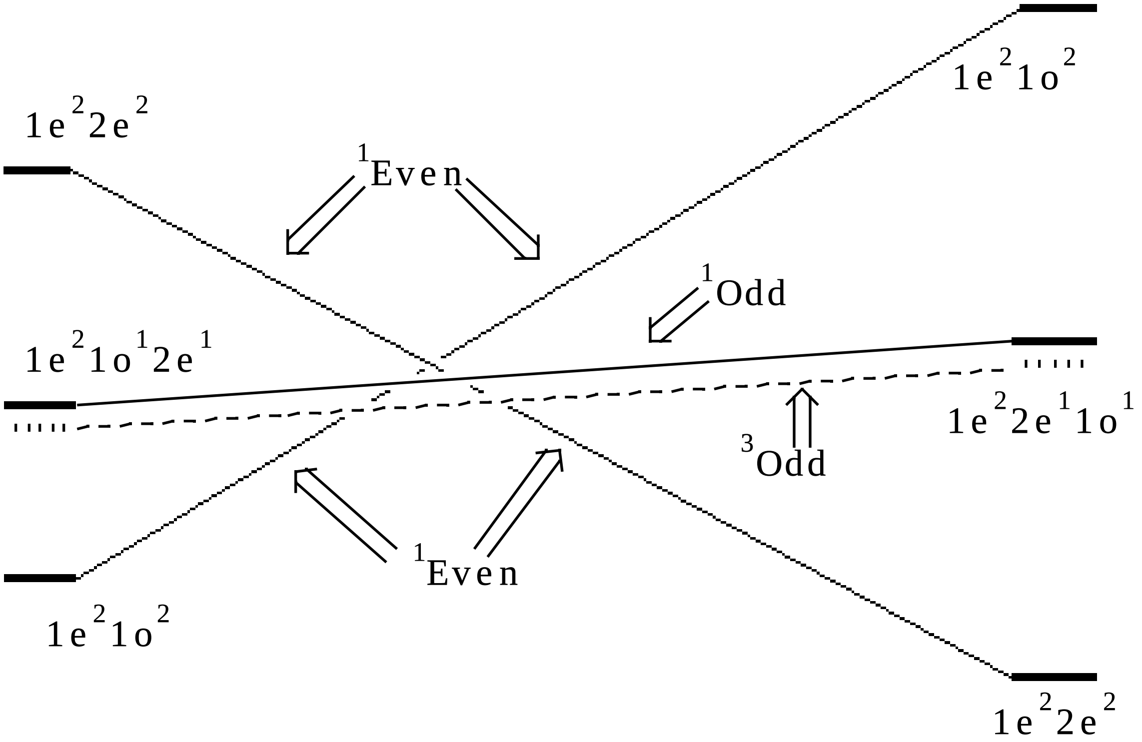
For the product molecule, on the other hand, the low-lying states are

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

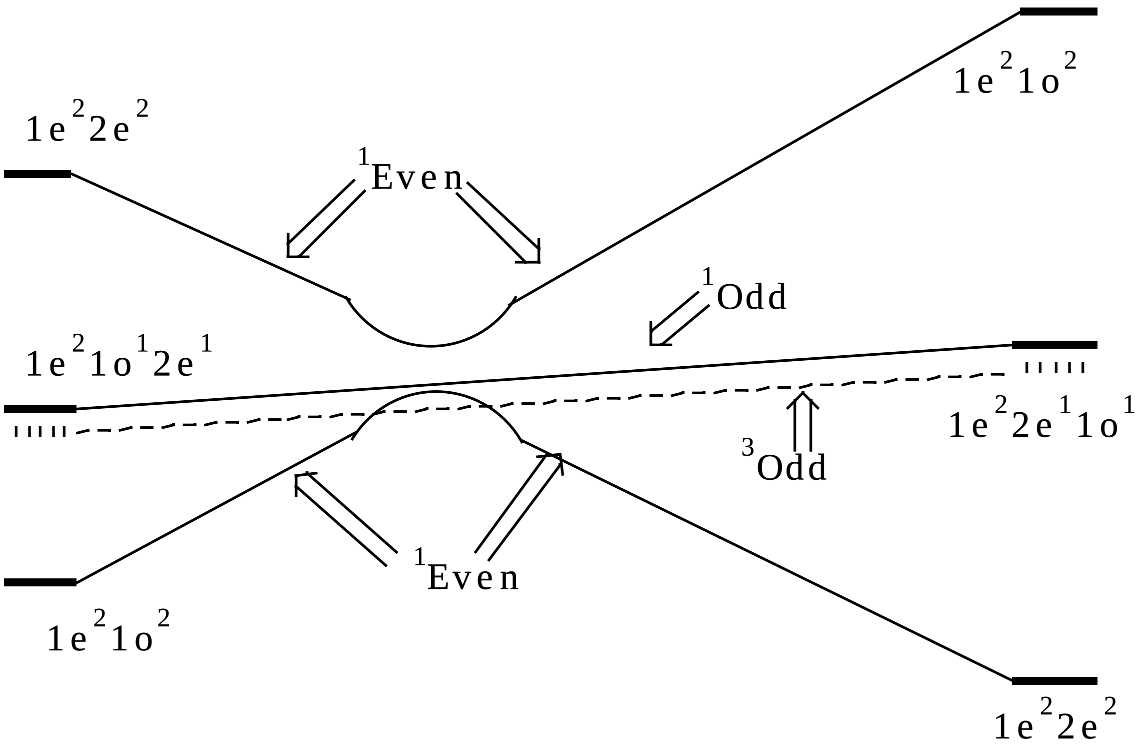
(iv) $\sigma^2\pi^1\pi\ ^1 = 1e^2 2e^1 1o^1$, ^{3}Odd , ^{1}Odd.

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 not 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 $1e^21o^2$ 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 $1e^22e^2$ 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 $1e^22e^11o^1$ 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:



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 symmety-imposed barrier 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 ππ 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 ππ surface this ^{1}Odd state intersects the ground ^{1}Even surface on the reactant side 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 product side 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 σ_g and antibonding σ_u mos appear.

There are two electrons that can both occupy the σ_g mo to yield the ground electronic state $H_2(^1\Sigma_g^+,\ \sigma_g^2)$; 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 $^1\Sigma_g^+(\sigma_u^2)$ 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 essential 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 lower 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 $^1\Sigma_g^+(\sigma_u^2)$ 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 $\sigma^2 d^n d^{n+1}$ 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^1d^{n+1}) + M^+ (s^1d^n). For most metals, this dissociation asymptote lies higher in energy than the heterolytic products X: + Y = M (s^2d^n) + M^+ (s^0d^{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^0d^{n+1} configuration) and a two electron donor, L : . A prototype is $(Ag\ C_6H_6)^+$ which was observed to photodissociate to form X· + Y· = Ag(^{2}S, s^1d^{10}) + $C_6H_6^+(^2B_1)$ rather than the lower energy (heterolytically cleaved) dissociation limit Y + X: =
$Ag^+(^1S,\ s^0d^{10}) + C_6H_6\ (^1A_1)$.

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 σ^2 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 $(\sigma^*)^2$ CSF is given by

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

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:

$$^1\Sigma^*\ (0) = \frac{1}{\sqrt{2}}\ [\ \text{½}\sigma\alpha\sigma^*\beta\text{½} - \text{½}\sigma\beta\sigma^*\alpha\text{½}]$$

is the singlet CSF and

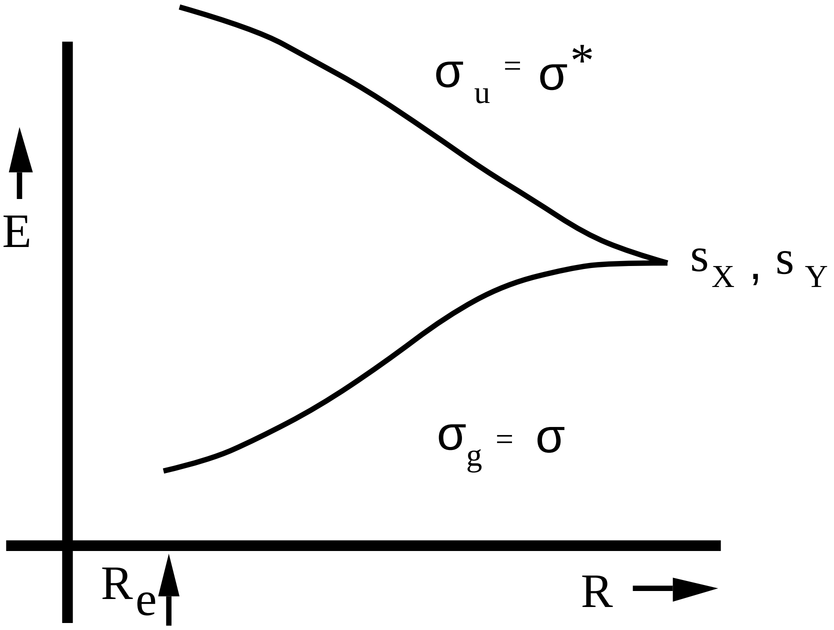
$$^3\Sigma^*\ (0) = \frac{1}{\sqrt{2}}\ [\ \text{½}\sigma\alpha\sigma^*\beta\text{½} + \text{½}\sigma\beta\sigma^*\alpha\text{½}]$$

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

2. Orbital, CSF, and State Correlation Diagrams

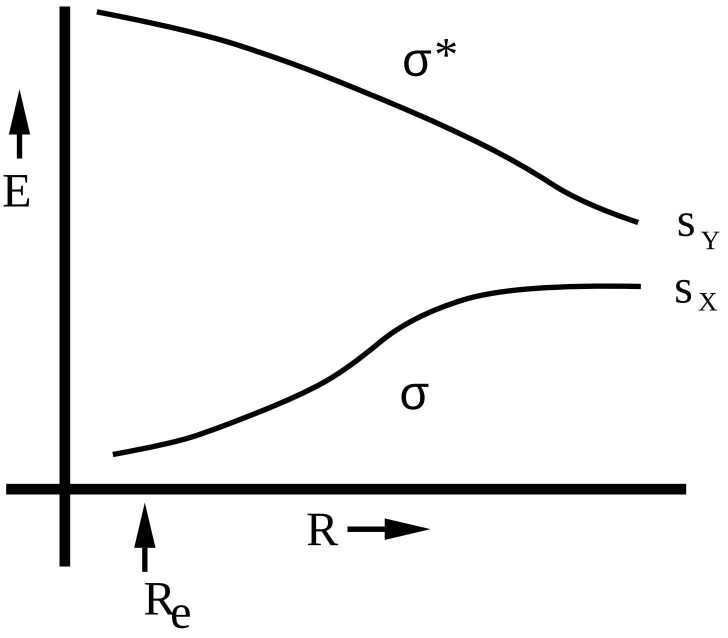
i. Orbital Diagrams

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 $\sigma = \sigma_g$ molecular orbital and an antibonding $\sigma^* = \sigma_u$ 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 σ and σ^* orbitals vary in a manner well known to chemists as depicted below.



Energies of the bonding σ and antibonding σ^* 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 σ and an antibonding σ^* 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 $R \rightarrow \infty$, 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 $R \rightarrow 0$, 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 not degenerate as $R \rightarrow \infty$. The energy "gap" between the σ and σ* orbitals at $R = \infty$ 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_I of the same symmetry must be combined to form the proper electronic eigenstates Ψ_K of the system:

$$\Psi_K = \sum_I C_I^K \Phi_I .$$

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_I^K of the CSFs Φ_I within each state Ψ_K are determined by solving the configuration-interaction (CI) secular problem:

$$\sum_J \langle \Phi | H | \Phi_J \rangle \; C_J^K = E_K \; C_I^K$$

for the state energies E_K and state CI coefficient vectors C_I^K. 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 $\langle \Phi | H | \Phi_I \rangle$ 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 σ^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 $R \rightarrow \infty$, the CSF energies $\langle \Phi | H | \Phi_J \rangle$ 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 $R \rightarrow \infty$ 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 σ and σ* into the Slater determinants that define the singlet and triplet CSFs can be illustrated as follows:

$$^1\Sigma(0) = |\sigma\alpha\ \sigma\beta| = C^2\ |(s_x + s_y)\ \alpha(s_x + s_y)\ \beta|$$

$$= C^2\ [|s_x\ \alpha\ s_x\ \beta| + |s_y\ \alpha\ s_y\ \beta| + |s_x\ \alpha\ s_y\ \beta| + |s_y\ \alpha\ s_x\ \beta|]$$

The first two of these atomic-orbital-based Slater determinants ($|s_x\ \alpha\ s_x\ \beta|$ and $|s_y\ \alpha\ s_y\ \beta|$) are denoted "ionic" because they describe atomic orbital occupancies, which are appropriate to the $R \rightarrow \infty$ region, that correspond to X: + Y and X + Y: valence bond structures, while $|s_x\ \alpha\ s_y\ \beta|$ and $|s_y\ \alpha\ s_x\ \beta|$ 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
$|\varphi_1\ \varphi_2\ \varphi_3| = -|\varphi_1\ \varphi_3\ \varphi_2|$, which implies that any determinant in which two or more spin-orbitals are identical vanishes $|\varphi_1\ \varphi_2\ \varphi_2| = -|\varphi_1\ \varphi_2\ \varphi_2| = 0$. The result of decomposing the mo-based CSFs into their atomic orbital components is as follows:

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

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

$$^3\Sigma^*(1) = |\sigma\alpha\ \sigma^*\alpha|$$
$$= CC^*\ 2|s_y\ \alpha\ s_x\ \alpha|$$

$$^{3}\Sigma^{*}\,(0) = \frac{1}{\sqrt{2}}\,[\,½\sigma\alpha\ \sigma^{*}\beta½ + \ ½\sigma\beta\ \sigma^{*}\alpha½]$$

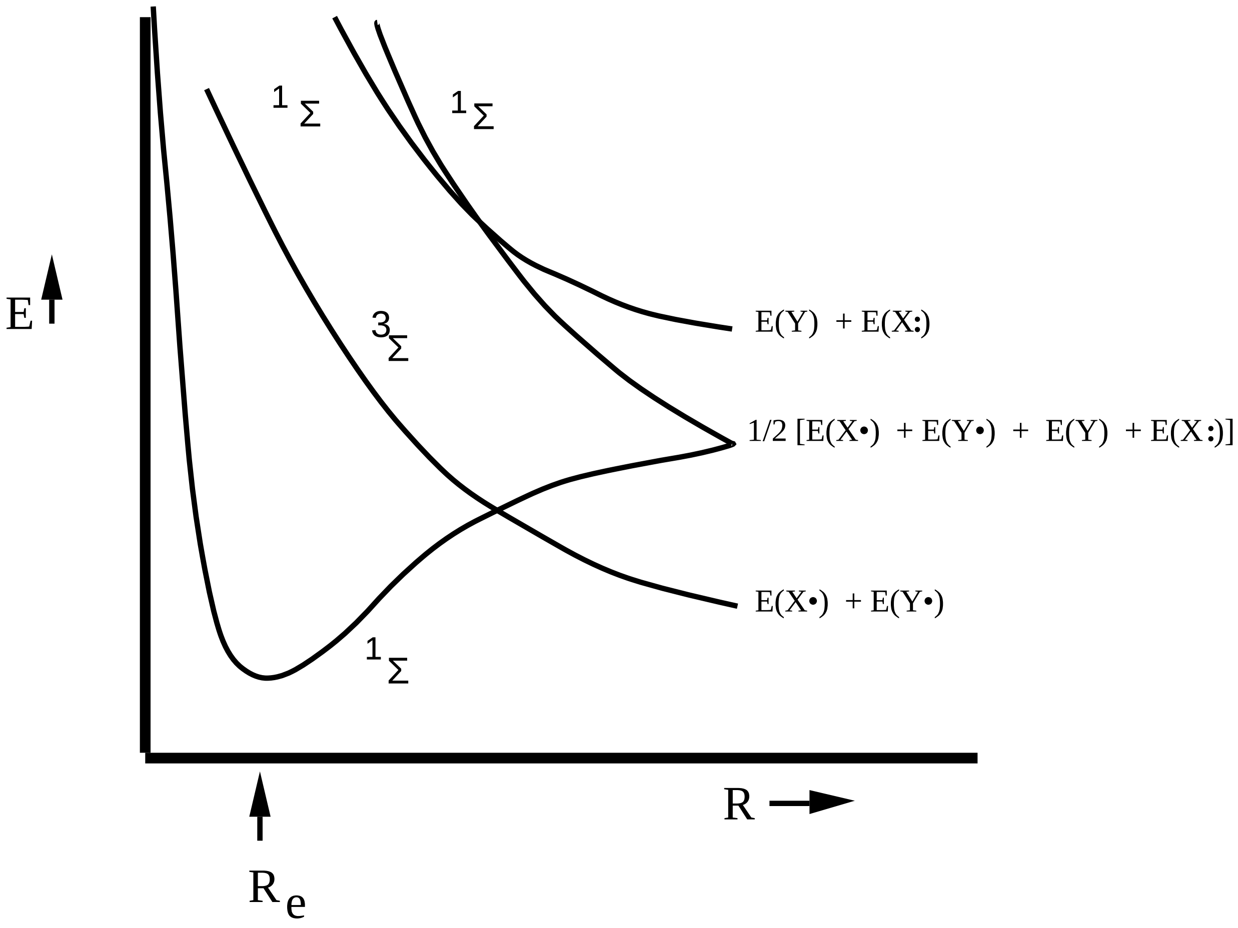
$$= CC^{*}\sqrt{2}\ \ [½s_{y}\ \alpha\ s_{x}\ \beta½ - ½s_{x}\ \alpha\ s_{y}\ \beta½]$$

$$^{3}\Sigma^{*}\,(-1) = ½\sigma\alpha\,\sigma^{*}\alpha½$$

$$= CC^{*}\ 2½s_{y}\ \beta\ s_{x}\ \beta½$$

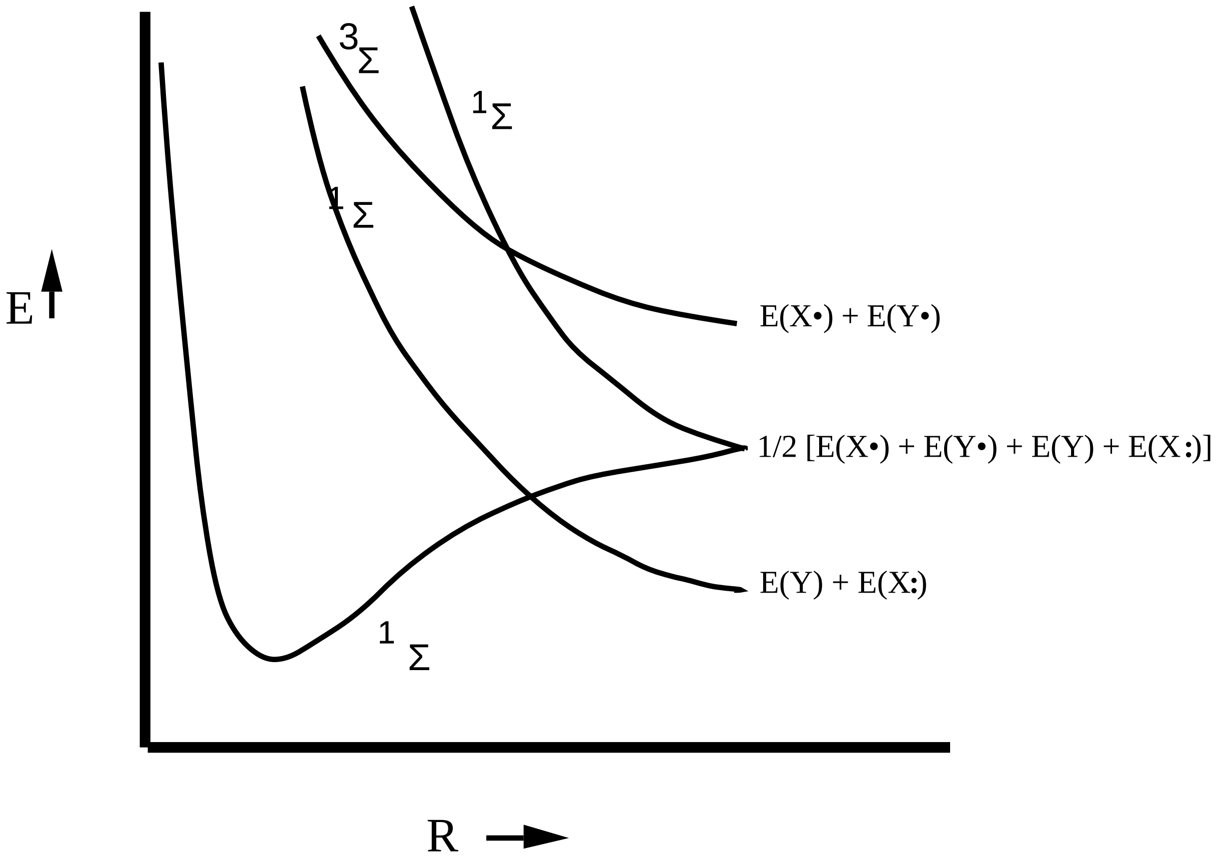
These decompositions of the six valence CSFs into atomic-orbital or valence bond components allow the R = ∞ energies of the CSFs to be specified. For example, the fact that both $^{1}\Sigma$ and $^{1}\Sigma^{**}$ contain 50% ionic and 50% covalent structures implies that, as R → ∞, both of their energies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



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

It is essential to realize that the energies $\langle\Phi|H|\Phi\rangle$ 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 $\langle\Phi|H|\Phi\rangle$ values; such is the case near R_e.

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

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

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:

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

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

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

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

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

The first solution thus has

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

which, when decomposed into atomic valence bond components, yields

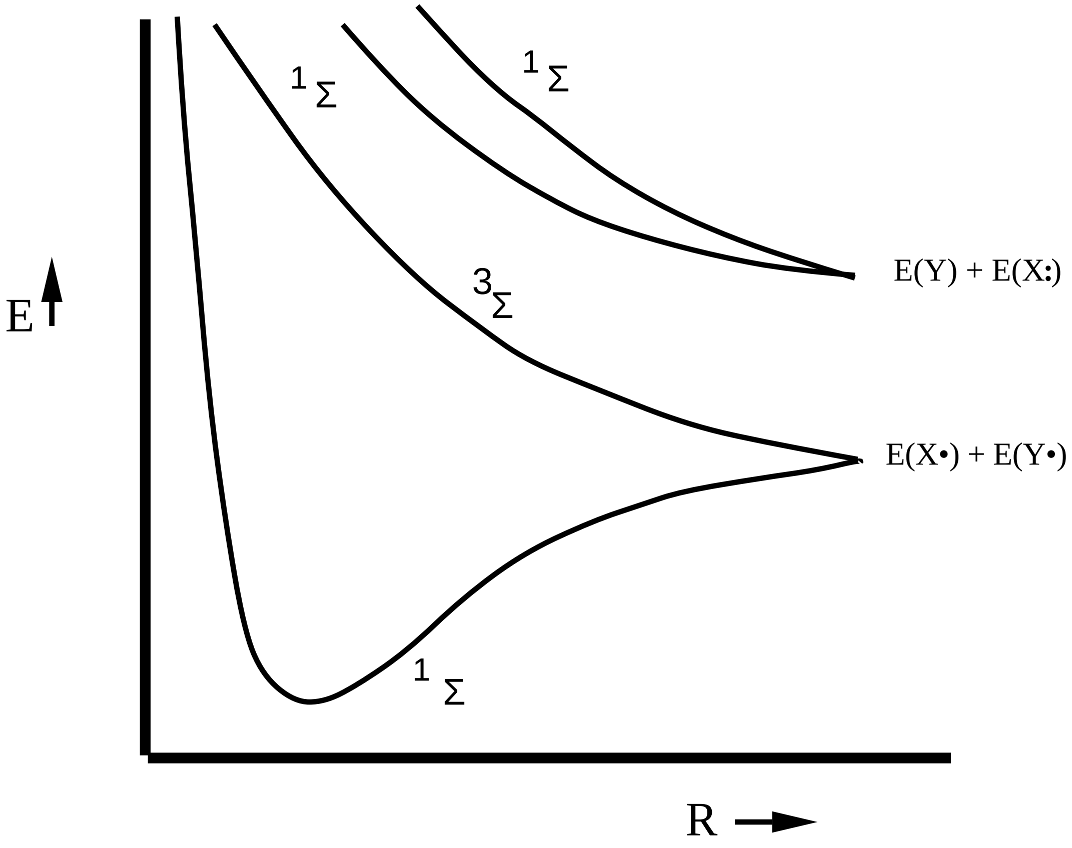
$$\Psi_- = \frac{1}{\sqrt{2}}\ [\ |s_x\alpha\ s_y\beta| - |s_x\beta\ s_y\alpha|].$$

The other root has

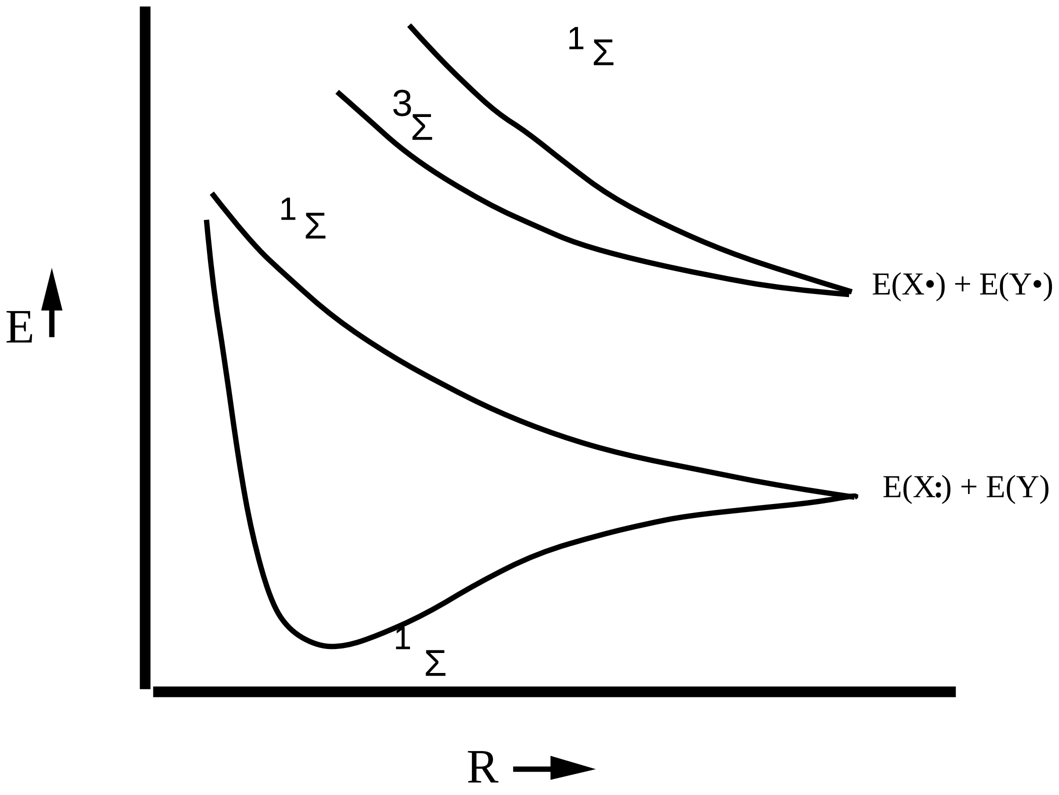
$$\Psi_+ = \frac{1}{\sqrt{2}}\ [|\sigma\alpha\,\sigma\beta| + |\sigma^*\alpha\ \ \sigma^*\beta|]$$
$$= \frac{1}{\sqrt{2}}\ [\ |s_x\alpha\ \ s_x\beta| + |s_y\ \alpha\ \ s_y\beta|].$$

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 Σ states 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 <u>heteronuclear</u> molecular orbitals introduced earlier yields:

$$^1\Sigma(0) = C^2 [½s_x\alpha\ s_x\beta½ + z^2 ½s_y\alpha\ s_y\beta½$$
$$+ z\ ½s_x\alpha\ s_y\beta½ + z\ ½s_y\alpha\ s_x\beta½]$$

$$^1\Sigma^{**}(0) = C^{*2} [z^2 ½s_x\alpha\ s_x\beta½ + ½s_y\alpha\ s_y\beta½$$
$$- z½s_x\alpha\ s_y\beta½ - z\ ½s_y\alpha\ s_x\beta½]$$

$$^1\Sigma^*(0) = \frac{CC^*}{\sqrt{2}} [2z½s_x\alpha\ s_x\beta½ - 2z\ ½s_y\alpha\ s_y\beta½$$
$$+ (z^2 - 1)½s_y\alpha\ s_x\beta½ + (z^2 - 1)\ ½s_x\alpha\ s_y\beta½]$$

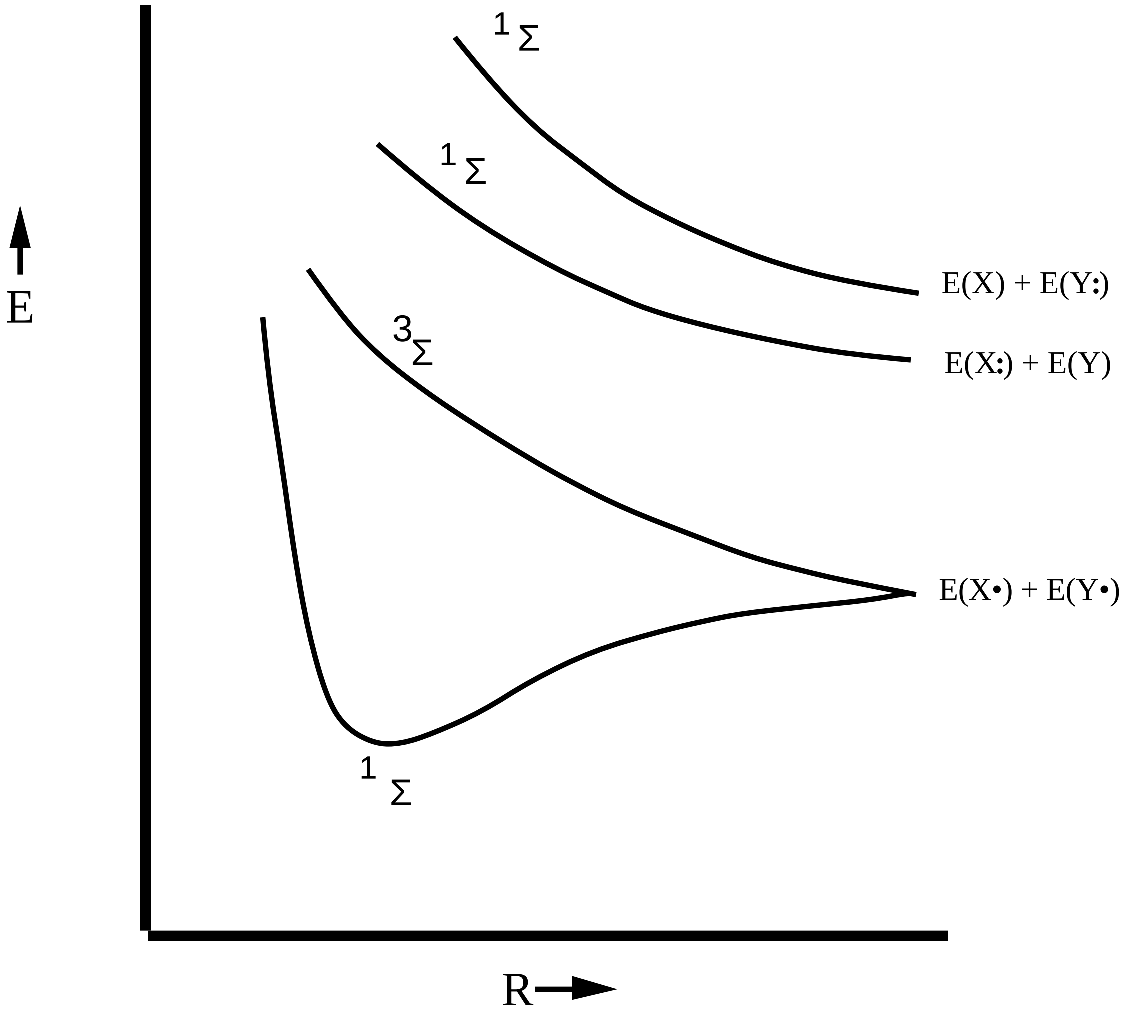
$$^3\Sigma^*(0) = \frac{CC^*}{\sqrt{2}} (z^2 + 1) \ [\text{½}s_y\alpha\ s_x\beta\text{½} - \text{½}s_x\alpha\ s_y\beta\text{½}]$$

$$^3\Sigma^*(1) = CC^* (z^2 + 1)\ \text{½}s_y\alpha\ s_x\alpha\text{½}$$

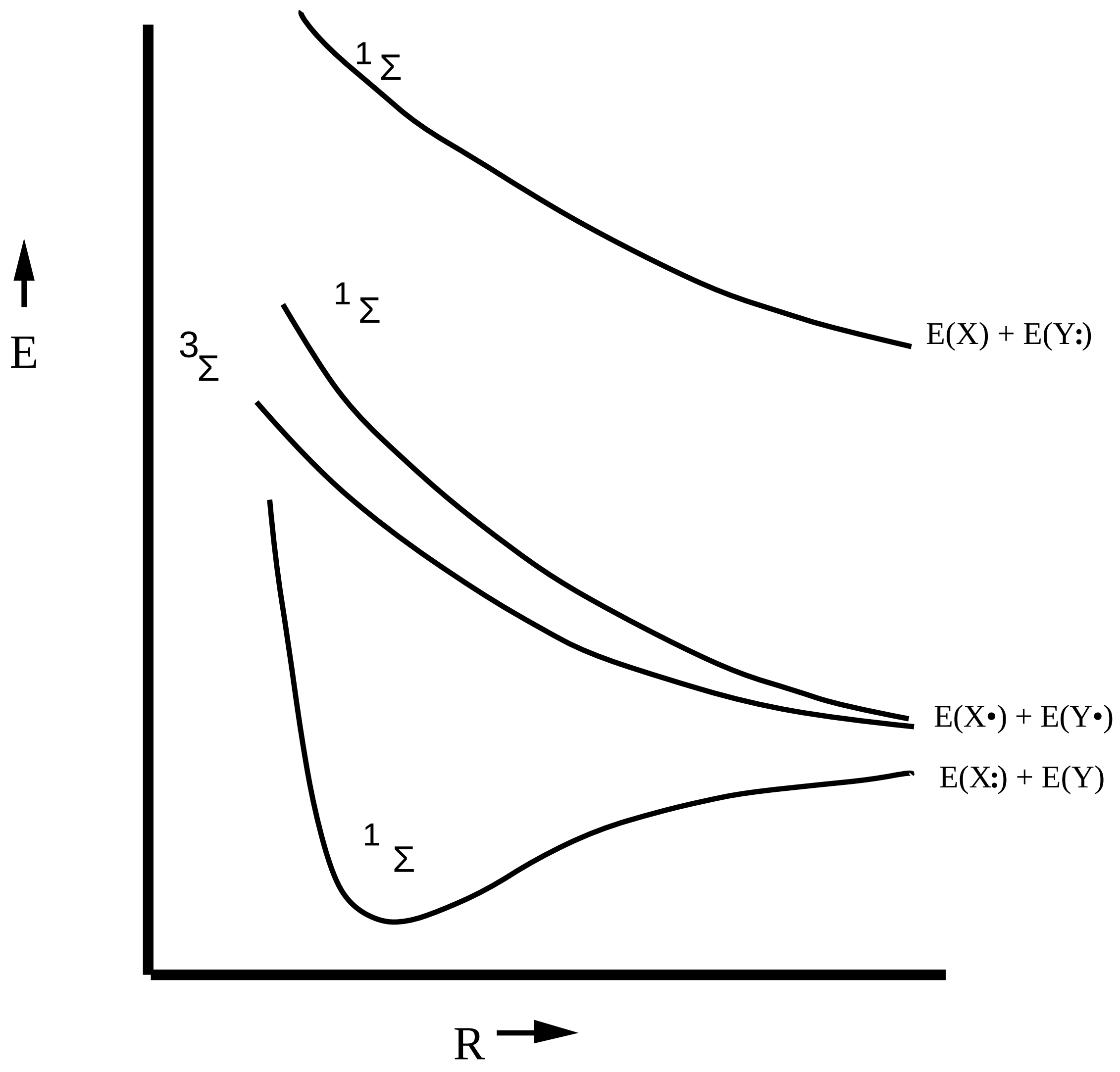
$$^3\Sigma^*(-1) = CC^* (z^2 + 1)\ \text{½}s_y\beta\ s_x\beta\text{½}$$

Clearly, the three $^3\Sigma^*$ 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 ½$s_x\alpha$ $s_y\beta$½+ ½$s_y\alpha$ $s_x\beta$½, ½$s_x\alpha$ $s_x\beta$½, and ½$s_y\alpha$ $s_y\beta$½. The three singlet CSFs therefore can be combined to produce a singlet covalent product function ½$s_x\alpha$ $s_y\beta$½+ ½$s_y\alpha$ $s_x\beta$½as well as <u>both</u> X + Y : and X : + Y ionic product wavefunctions ½$s_y\alpha$ $s_y\beta$½and ½$s_x\alpha$ $s_x\beta$½, respectively. In most situations, the energy ordering of the homolytic and heterolytic dissociation products will be either E (X·) + E (Y·) < E (X:) + E (Y) < E (X) + E (Y:) or E (X :) + E (Y) < E (X·) + E (Y·) < E (X) + E (Y :) .

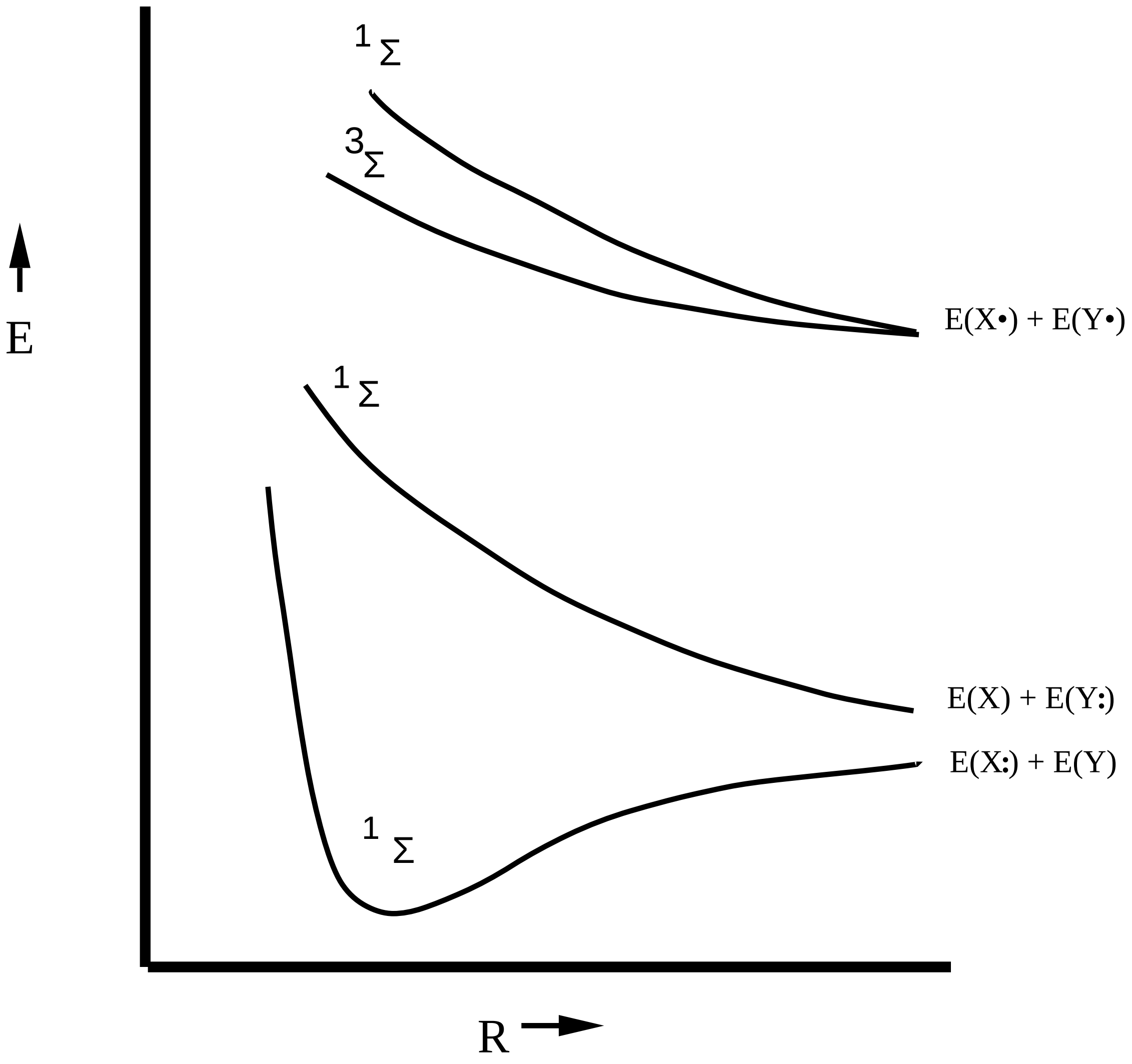
The extensions of the state correlation diagrams given above to the heteronuclear situations are described below.



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^2d^n (for first-row metals, exceptions include Cr (s^1d^5), Cu (s^1d^{10}), and the s^1d^9 state of Ni is basically isoenergetic with the s^2d^8 ground state). The corresponding positive ions have ground states with s^1d^n (Sc, Ti, Mn, Fe) or s^0d^{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, $M(s^2d^n) + M^+(s^0d^{n+1})$, than homolytic cleavage to $M(s^1d^{n+1}) + M^+(s^1d^n)$. For example, Co_2^+ dissociates to $Co(s^2d^7) + Co^+(s^0d^8)$ rather than to $Co(s^1d^8) + Co^+(s^1d^7)$,[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 $Co(s^2d^7) + Ni^+(s^0d^9)$. The alternative heterolytic cleavage to form $Co^+(s^0d^8) + Ni(s^2d^8)$ is 0.23 eV higher in energy, while homolytic cleavage can lead to $Co^+(s^1d^7) + Ni(s^1d^9)$, 0.45 eV higher, or $Co(s^1d^8) + Ni^+(s^1d^8)$, 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:

$$\Psi = \Sigma_I C_I \Phi_I ,$$

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:

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

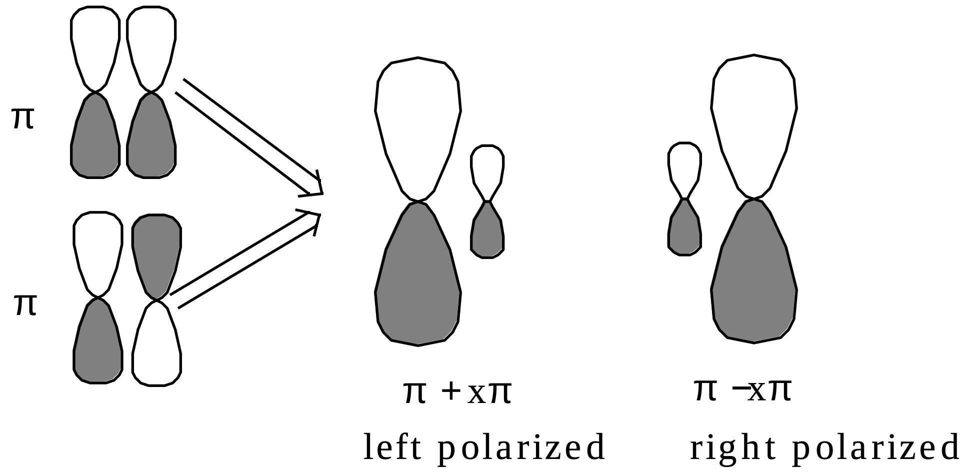
$$= C_1/2 \{ | ..(\phi - x\phi')\alpha (\phi + x\phi')\beta..| - | ..(\phi - x\phi')\beta (\phi + x\phi')\alpha..| \},$$

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 ($\varphi - x\varphi'$) and ($\varphi + x\varphi'$). 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. 29, 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 π and π^* orbitals to produce two left-right polarized orbitals as depicted below:



In this case, one says that the π^2 electron pair undergoes left-right correlation when the $(\pi^*)^2$ 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 Ψ can place electron pairs, 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 "<u>dynamical electron correlation</u>"; they are extremely important to include if one expects to achieve chemically meaningful accuracy (i.e., ± 5 kcal/mole).