12.2: 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 ($e.\,g.\,, X\cdot, Y\cdot, X, Y:, etc.$), 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 $X\cdot$ and $Y\cdot$ 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.

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 sg and antibonding su mos appear. There are two electrons that can both occupy the sg mo to yield the ground electronic state $H_2(1S_g^+, S_g^2)$; however, they can also occupy both orbitals to yield $^3Su + (sg^1s_u^1)$ and $^1S_u + (s_g^1s_u^1)$, or both can occupy the su mo to give the 1Sg +(su 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.

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 $^1\sum_u^+(\sigma_g^1\sigma_u^1)$ and $^1\sum_g^+(\sigma_u^2)$ 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 s bond is formed primarily from the metal atom s orbitals. If the σ bond is homolytically broken, one forms $X\cdot + Y\cdot = M(s^1 d^{n+1}) + M^+(s^1 d^n)$. 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 $X\cdot + Y\cdot = Ag(^2S, s^1 d^{10}) + C_6 H_6 + (^2B_1)$ rather than the lower energy (heterolytically cleaved) dissociation limit Y + X: $= Ag^+(^1S, s^0 d^{10}) + C_6 H_6(^1A_1)$.

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

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

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

suffices. An analogous expression for the $(\sigma^*)^2$ CSF is given by

$$^1\sum^{**}(0) = |\sigma^*\alpha\sigma^*\beta| = \frac{1}{\sqrt{2}}\left[\sigma^*\alpha(1)\sigma^*\beta(2) - \sigma^*\alpha(2)\sigma^*\beta(1)\right].$$

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