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Some Additional Clarifications on the Concept of Rydbergization and Avoided Crossings

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Recently, Malrieu published an extensive review article [1] which, in part, dealt with the representations of Rydberg states. We have recently [2, 3] examined the theoretical aspects of Rydberg photochemistry of small molecules and reexamined the question of avoided crossings in the NH bond rupture surfaces of ammonia [4] as viewed from MO theory. Since none of these publications were available to Malrieu at the time his manuscript was submitted for publication, he was not acquainted with our approach to the problem. In particular, a superficial comparison of our respective approaches might produce the false impression that there is a fundamental difference of view on the subject of Rydbergization [5, 6]. Malrieu dealt with two different types of Rydbergization. The type which we will not deal with here results from the avoided crossing of two real surfaces which have differing valence-Rydberg characters. This type of Rydbergization is usually theoretically described by the CI mixing of two configurations differing by two spin orbitals (e.g. O_2, Cl_2, [7]). The other type, MO-Rydbergization [5, 6], occurs at orbital level and can be correlatively treated at the SCF level for a particular state provided that the state is MO-dissociating [5, 6]. A thorough understanding of the theoretical aspects of this type of Rydbergization is necessary if one is to understand the threshold photochemistry of ammonia, water, alkanes, and related organics [2, 3]. While Malrieu expressed the idea that this type of Rydbergization is treatable at the single configuration MO level, he also stated that it occurs when a (h/R) Rydberg state *mixes* with a (h'/V^*) valence (antibonding) state in which the holes, h and h', are qualitatively the same. This latter view had been previously criticized by Mulliken [5, 6] with regard to the rationalization of the Rydbergization of the π^* orbital in the $^1\pi\pi^*$ excited state of ethylene. Our goal here is to conceptually resolve this conflict and to show under what conditions Malrieu's statement is correct. We will use the NH bond rupture surface in NH_3 as an example.

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We have recently reviewed the question of avoided crossings in the NH bond rupture surfaces of ammonia and demonstrated that the Rydbergization of the lowest excited state of planar NH_3 ($^1A_2''$, $n \rightarrow 3s$) can not be diagrammatically or computationally attributed to an avoided crossing between a Rydberg and valence state [4]. However, the conceptual idea that such an avoided crossing is responsible for the derydbergization of the excited state surface as it evolves to the valence states of the NH_2 $(1^2B_1)+H(^2S)$ radical products has general acceptance among experimentalists [8–10]. Likewise, theoretical chemists have invoked avoided crossing arguments in rationalizing similar Rydbergizations occurring on the threshold excited state surfaces in methane [11] and methanol [12]. These surfaces are correlatively identical to the NH_3 surface [2, 3] and the Rydbergizations are due, in SCFMO theory, to changing Rydberg character of a particular MO [13]. In the case of NH_3, the $4a_1$ MO has conceptually mixed valence-Rydberg character ($c_1 3s_N + c_2 1s_H$) varying from being almost totally $3s_N$ at the NH_3 configuration to $1s_H$, localized on the departing H atom, at the $NH_2 + H$ diradical limit [13]. This particular MO-Rydbergization can be alternatively viewed as resulting from an avoided MO-crossing [14]. However, we have shown this concept to be base orbital dependent [4]. In any case, according to SCFMO theory, no avoided state crossings are involved in this type of Rydbergization.

Although the above arguments seem to have rejected the idea of avoided state crossings in order to rationalize what is otherwise viewed as MO-Rydbergization, we will now show that within the context of valence bond theory, the idea is quite acceptable. We have previously constructed the Rydberg expanded orbital and state correlations diagrams for NH_3 [4]. Fig. 1 shows a truncated VB state correlation diagram for the C_{2v} NH bond rupture pathway in planar NH_3. Only the symmetries of critical interest are shown. Of those structural representations shown for NH_3, only the ground state (1^1A_1 in C_{2v}, $1^1A_1'$ in D_{3h}) and the 1^1B_1 and 2^1B_1 ($1^1A_2''$ and $^1E''$, respectively in D_{3h}, see Refs. [4, 12]) are real. The hypothetical $n \rightarrow \sigma^*$, $n\,^1B_1$ state has no known physical or large basis set computational existence [4]. However, all the NH_2 radical states shown in Fig. 1 have physical existence [15]. The before mixing correlation between the NH_3 and $NH_2 + H$ states (dotted lines) is established on the basis of the apparently identical AO basis set composition of the structures. The after mixing correlations are shown by solid lines, the avoided crossing points shown by large dots.

While we are mainly interested in the derydbergization of the 1^1B_1 surface of $NH_3 - NH_2 + H$, we must first discuss the problem of the ground state NH rupture (1^1A_1). This is a simple σ-bond rupture which in VB theory can be *correlatively* treated at the single configuration level using nonionic structures (i.e. $\Psi(1^1A_1) = [1^2A_1][H]$). Therefore, simple σ-bond, $A{:}B$, will diagrammatically yield the radical pair, $A\cdot + \cdot B$, without an avoided VB crossing. In contrast, an MO correlation diagram, will yield an avoided diradical-ionic crossing [3, 4] which will computationally require at least a two configurational (SCF-CI, MCSCF) description of the avoided crossing region and the diradical limit (in certain types of MCSCF treatments). Therefore, one already sees that what is viewed as

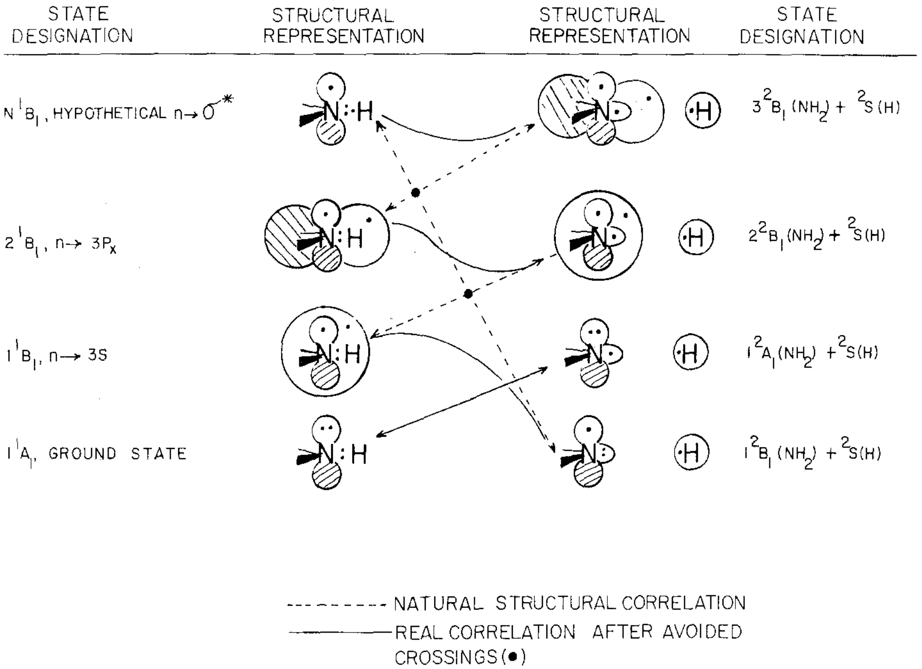

Fig. 1. Shown are the structural representations of the various real and hypothetical states of NH_3 and $NH_2 + H$. The large orbitals are either $3s$ or $3p_x$ Rydbergs where the x axis represents the C_{2v} pathway for NH bond rupture in planar NH_3.

non-crossing in a VB state correlation diagram is a crossing phenomenon in MO theory. In any case either this direct VB correlation or an avoided MO correlation [4] shows that the ground state of NH_3 directly correlates with the 1^2A_1 $(NH_2)+$ $H(^2S)$ diradical pair. This rules out any speculation [1, 12] that an excited NH_3 state may correlatively yield the same diradical pair.

With regard to the B_1 states, Fig. 1 shows the before crossing natural structural correlations: $1^1B_1(NH_3) \leftrightarrow 2^2B_1(NH_2) + H(^2S)$; $2^1B_1 \leftrightarrow 3^2B_1 + H$; and $n\,^1B_1 \leftrightarrow$ $1^2B_1 + H$. The first two correlations involve the formation in valence space of a two electron N—H bond, a highly exothermic situation as viewed from the diradical limit (right-to-left). However, the latter correlation is repulsive in character, placing three electrons in the same valence space (two of which have the same spin). Therefore, the latter correlation will cross with the other two, and the final correlation occurs, as it must numerically (i.e. $m\,^1B_1(NH_3) \leftrightarrow$ $m\,^2B_1(NH_2) + H$), as shown in Fig. 1. In the VB diagram the derydbergization of the 1^1B_1 surface occurs because of an avoided crossing of two VB structural configurations, one having valence and the other Rydberg character. Note, however, that there is required no hypothetical existence of a real valence excited state. The next avoided crossing yields a correlation of a $n \rightarrow 3p_x$ $(NH_3) \leftrightarrow n \rightarrow$ $3s(NH_2) + H(^2S)$ in which the role of the valence component is problematical. Likewise, the addition of other Rydberg components ($4s$, $5s$, etc) will cause a progressive dilution of the possible role of a valence component in the upper excited states. This can be described in the approximate wavefunction: $\Psi(^1B_1$ surfaces) $= c_1[1^2B_1][\mathrm{H}]+c_2[2^2B_1][\mathrm{H}]+c_3[3^2B_1][\mathrm{H}]+c_n[n^2B_1][\mathrm{H}]$+ionic and H-Rydberg components. A truncated form can be used to describe the behavior of the 1^1B_1 surface: $c_1[1^2B_1][\mathrm{H}]+c_2[2^2B_1][\mathrm{H}]$. In this case the changing Rydberg character along the 1^1B_1 surface results from changing values of c_1 and c_2 generated by an avoided crossing of the two VB configurations. Note that this truncated solution does not imply that there exists another real surface having the conjugate solution: $c_2[1^2B_1][\mathrm{H}]-c_1[2^2B_1][\mathrm{H}]$. Such a conjugate solution may be deceptively obtained if the Rydberg basis set is too small [4].

The conditions under which this type of Rydbergization will appear to be due to an avoided state crossing are varied. Diagrammatically, it will not appear if one correctly uses molecular orbital correlations diagrams to prepare the final correlation diagrams [4]. In this case the Rydbergization occurs at the *MO* level [4, 14]. Likewise, if the particular open shell SCF configurational state is a good description of the molecular state in question along the entire surface, as is the case in the $n3s$ state of NH_3 [4, 13], no avoided crossings will be computationally observed. However, if the MO's in question are not SCF for the state in question, one will observe an avoided crossing behavior due to CI mixing of monoexcited configurations differing by only one spin orbital (e.g. see Ref. [11]). This mixing will become apparently increasingly stronger as the MO's in question become increasingly non-SCF. Therefore, the effect should be very strong if one does CI on configurations constructed from either symmetry orbitals or the base orbitals themselves. Since, under full CI all these variations are identical, it is equally valid to view this type of Rydbergization as resulting from either MO-Rydbergization or mixing of configurations (non-SCF or VB in type) having principally either valence or Rydberg character. The only conceptual precaution is to avoid assigning real physical existence to either these premixed configurations or to MO correlation diagrams.

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15. Peyerimhoff, S. D., Buenker, R. J.: Can. J. Chem. **57**, 3182 (1979). Note that our Figure 1 is a simplification as to the actual 3^2B_1 state in NH_2. The three open shell characters of our 2^2B_1 and 3^2B_1 configurations actually permit a total of four not two surface correlations. Figure 1 shows only the bonding correlations.

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