

Avoided Crossings in Excited States Potential Energy Surfaces

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Abstract: The potential energy barriers which govern the kinetic feasibility of photochemical reactions result from avoided crossing between states of similar symmetry. The first type of avoided crossing, as investigated by Salem, is induced in general by the allowed crossing of MOs of different symmetry and intervenes only at the states level. The second, illustrated here in the *ab initio* SCF-CI calculated potential energy surfaces for the *n*- and π -initiated hydrogen abstraction by carbonyl groups, is a direct consequence of avoided crossings between MOs of identical symmetry. The memory of the MOs intended or "natural" correlations shows up—via pseudoavoided crossings of the electronic states—as barriers or wells in the excited states potential energy surfaces.

A factor which is often encountered in determining the kinetic feasibility of a photochemical reaction is whether sufficient activation energy to drive the reaction can be effectively achieved during the lifetime of the potentially reactive excited state, that is, the rate of reaction relative to the rates of excited state deactivation by radiative or radiationless processes is of primary importance. Note immediately the order of magnitude of these activation energies. For an unimolecular or bimolecular reaction to compete, in a singlet state, with fluorescence, its activation energy should be in the 6–9 and 0–3 kcal/mol ranges, respectively. For similar processes to compete, in a triplet state, with phosphorescence these numbers become larger: 14–18 kcal/mol for a unimolecular reaction and 7–11 kcal/mol for a bimolecular event.² An important point at issue in the construction of theoretical potential energy surfaces (PES) is then to be able to *predict* the existence of energy barriers, and, in particular, *small* energy barriers.

Barriers in the low-lying excited states PES of a reacting system arise from avoided crossings between states of similar symmetry.³ In other words, these barriers show up as the memory of the intended or "natural" correlations of these states. A typical MO pattern inducing such an avoided crossing is schematized in a two-electron, four-orbital model (Figure 1a). The symmetric (S) or antisymmetric (A) character refers to the behavior of the MOs with respect to a given (unspecified) symmetry operation. The high-lying $(1S)^1(2S)^1$ state of the reactants continuously decreases in energy and correlates with the low-lying $(1S)^1(2S)^1$ state of the intermediates (Figure 1b). At the same time the $(1A)^1(2A)^1$ state of the reactants correlates with the $(1A)^1(2A)^1$ state of the intermediates (or products). The "natural" crossing of the two curves is symmetry forbidden. The final correlation of the $(1A)^1(2A)^1$ state of the reactants with the $(1S)^1(2S)^1$ wave function of the intermediates is characterized by (a) the conservation of the overall electronic symmetry but (b) a simultaneous switch of both electrons from A to S MOs. This analysis accounts for the barriers encountered in the $^3\pi\pi^*$ photodecomposition of toluene into a hydrogen atom and a benzyl fragment^{3b,4} and in the $^1\pi\pi^*$ elongation of a CH linkage in formaldehyde (α -cleavage).⁵ Let us emphasize that, in this first situation, the avoided crossing occurs between a pair of *states* and that the "natural" correlation of the S and A MOs which induces it is unperturbed by the SCF part of the calculation which treats independently the orthogonal A and S manifolds.

Imagine, however, a pair of MOs of identical symmetry which would tend to intersect each other in the course of a reaction. The resultant mixing will be solved for in the SCF step of the calculations. Barriers or wells in the MOs potential energy curves will eventually appear as the last remnants of the

intended but avoided crossing. This in turn will lead to barriers (or wells) in the states PESs. Of course these perturbations will be rather small but their mechanistic importance is not to be underestimated given the limited activation energy an excited state can acquire during its lifetime. In the course of our systematic theoretical study⁶ of hydrogen abstraction by ketones we have encountered several examples of this second family of potential energy barriers.

Let us first consider the *n*-initiated hydrogen capture in a simple formaldehyde–methane model. A CH methane bond is broken, an OH counterpart formed. The bonding σ CH MO, destabilized during the elongation of the CH linkage, would finally correlate with the sp^3 hybrid on the methyl moiety (σ_{CH_3}). At the same time the OH σ bonding orbital is built via the progressive interaction of the oxygen lone pair (*n*) and the 1s hydrogen atomic orbital which is gradually released by the rupture of the CH bond. This means that *n* would naturally be stabilized and correlate with σ_{OH} . The crossing between these two in-plane orbitals is strongly avoided, and, as a result, the final correlation links *n* and σ_{CH_3} on one hand, σ_{CH} and σ_{OH} on the other^{3b} (Figure 2a). A state correlation diagram based on these final SCF MOs would directly join the $^1,^3n\pi^*$ states of the reactants and the $^1,^3D_{\sigma\pi}$ diradical states⁹ of the intermediates. However, such a straightforward reasoning would bypass the consequences of the natural or intended correlations of the MOs, that is, the fact that the $n\pi^*$ states would wish to reach high-lying $\sigma_{OH}\rightarrow\pi^*$ excited states of the zwitterionic $CH_2OH^+ + CH_3^-$ intermediates⁹ (Z_1) while the $D_{\sigma\pi}$ states come from a high-lying charge transfer $\sigma_{CH}\rightarrow\pi^*$ state of the reactants (Figure 2b). There is no avoided crossing *stricto sensu* between these two PESs since the MOs crossing has already been taken into account at the SCF stage of the calculations but the memory of the intended MOs correlations still appears as a small barrier in the $^1,^3n\pi^*$ states PES (9.2 and 4.6 kcal/mol for the triplet and singlet states, respectively) and a deeper potential well in the corresponding charge-transfer PESs (~ 30 kcal/mol) (Figure 3).¹¹ Finally let us remark that the pseudoavoided crossing of the states corresponds physically to the exchange of one electron between MOs of similar symmetry, that is, from *n* to σ_{CH} (or σ_{OH} to σ_{CH_3}).

The second example we wish to discuss is the π -initiated hydrogen abstraction reaction, again in the simple methane–formaldehyde system in which the captured hydrogen atom ends up at the carbon center of the carbonyl chromophore thus producing methoxy and methyl groups.¹² The calculated MO pattern is represented in Figure 4a. The bonding π_{CO} function which is already localized at the oxygen end of the carbonyl correlates with a pure p orbital of the alkoxy oxygen atom (n'_o).¹³ The mixing of the three remaining in-plane MOs (σ_{CH} ,

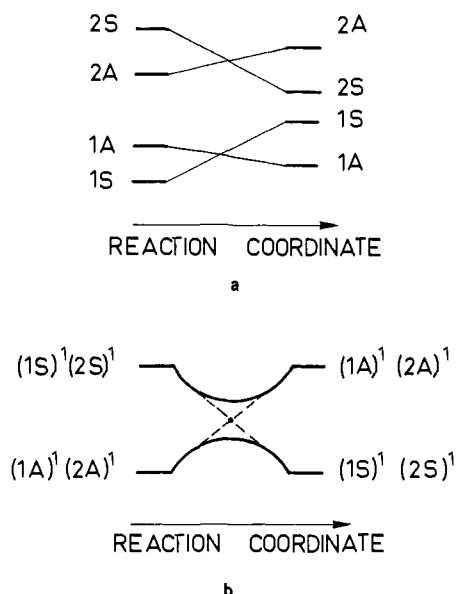


Figure 1. (a) Symmetry-allowed crossings of A and S MOs in the four-orbital two-electron model. (b) Symmetry-forbidden crossing of totally symmetric excited wave functions.

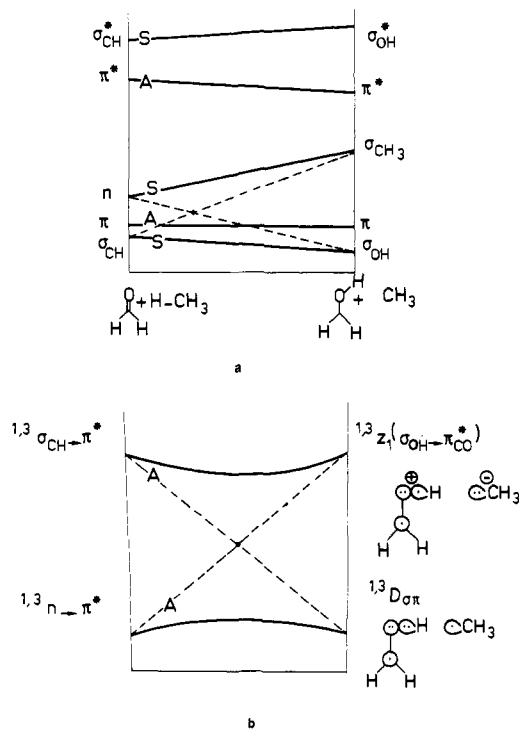


Figure 2. (a) Calculated MO correlation diagram in the n-initiated hydrogen abstraction in the formaldehyde-methane system.¹⁰ (b) "Natural" behavior of the $n\pi^*$ and $\sigma_{CH}\pi^*$ excited states of the formaldehyde methane system during the abstraction.¹⁰

σ_{CH}^* , and π_{CO}^*) is continuous but involves an intended crossing which is erased at the SCF stage of the calculations. Indeed π_{CO}^* which is mainly concentrated on the carbon atom tends to form the antibonding σ_{CH}^* orbital and is therefore destabilized. The σ_{CH}^* methane MO is stabilized by the elongation of the CH linkage (its antibonding character decreases) and—were it not for the avoided nature of its intersection with π_{CO}^* —would correlate with the sp^3 -like orbital of the methyl moiety (σ_{CH_3}). Using the final SCF MOs one would predict a straight correlation of the pair of $^{1,3}n\pi^*$ states of the reactants with the $^{1,3}D_{\sigma\pi}$ diradical states of the inter-

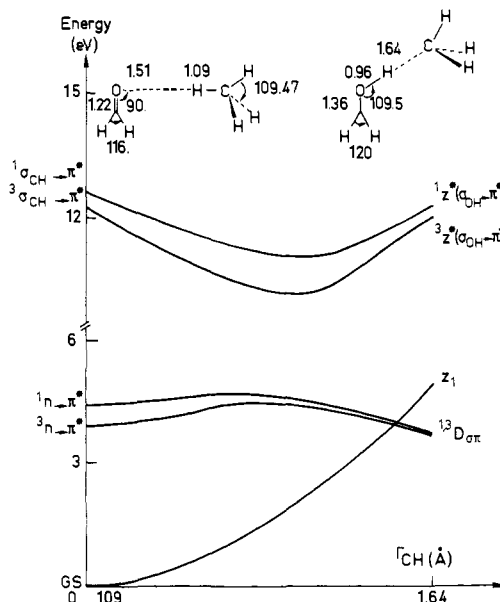


Figure 3. Calculated potential energy curves in the n-initiated hydrogen abstraction in the formaldehyde-methane system (in the starting and final geometries the bond lengths and angles are in ångströms and degrees, respectively).

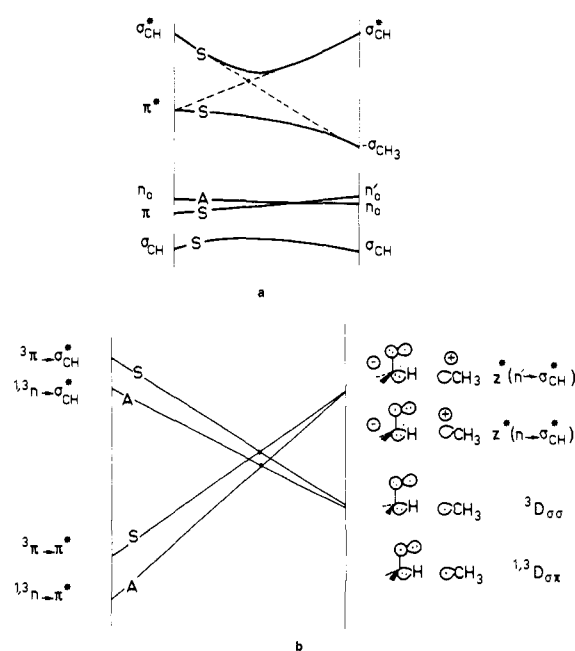


Figure 4. (a) Calculated MO correlation diagram in the $\pi(C)$ initiated hydrogen capture in the formaldehyde-methane system.¹⁴ (b) "Natural" behavior of the $n\pi^*$ and $\pi\pi^*$ excited states.¹⁴

mediates on one hand, and of the $\pi\pi^*$ triplet with the $D_{\sigma\sigma}$ triplet diradical on the other. Though the gross behavior of the states would be correctly explained, this analysis overlooks the fact that, for these three states, an additional energy barrier exists which is due to the natural correlations of the antibonding MOs. If one considers this natural evolution it appears that the $n\pi^*$ and $\pi\pi^*$ states correlate with (degenerate) excited functions of the zwitterionic intermediates $CH_3O^- + CH_3^+$ ($n \rightarrow \sigma_{CH}^*$ and $n' \rightarrow \sigma_{CH}^*$, respectively). At the same time the $D_{\sigma\pi}$ and $D_{\sigma\sigma}$ states are linked with high-lying charge-transfer forms of the reactants (namely, $n \rightarrow \sigma_{CH}^*$ and $\pi \rightarrow \sigma_{CH}^*$, respectively) (see Figure 4b).¹⁴ Of course, the resulting pseudoavoided crossings are strongly prevented by the mixing which has already intervened at the MO-SCF level. Still the system conserves some memory of it in the energy barriers (~ 20

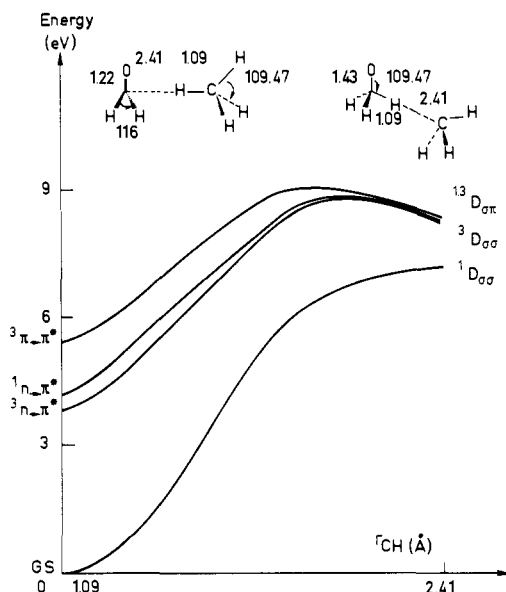


Figure 5. Calculated potential energy curves in the $\pi(C)$ initiated hydrogen abstraction in the formaldehyde–methane system (in the starting and final geometries the bond lengths are measured in ångströms, the angles in degrees).

kcal/mol) which are superimposed on the quasi-linear ascending energy changes suggested by the final MO correlations (Figure 5). Note that the $n\pi^* \rightarrow D_{\sigma\pi}$ and $\pi\pi^* \rightarrow D_{\sigma\pi}$ correlations require the (charge-transfer) jump of one electron from the π^* to the σ^*_{CH} function.

Two types of avoided crossings therefore govern the morphology of excited states PESs. The first, as discussed by Salem,⁵ occurs at the *states level* and is initiated at the MO stage by the allowed crossing (s) of MOs of different symmetry. The second, as illustrated in the preceding examples, already occurs at the *MO stage* and involves MOs of identical symmetry. The discussion of the natural correlations of the states is only a convenient—and formal—way to clarify the additional barriers (or wells) which may appear in the surfaces. Let us again insist that the rationale behind these features is to be looked for at the MO level. The mechanistic importance of these two types of crossings is comparable. Both usually result in small barriers (<20 kcal/mol) but the major role such barriers play in the kinetic feasibility of photochemical reactions makes their prediction a key factor in our understanding of the behavior of excited species. While the first type (states avoided and MO allowed crossings) is easily detected by simply looking at the MO pattern obtained at the SCF stage, the second (MO and states avoided crossings) requires a careful understanding of the MO's “natural” correlations or, in other words, of “where the MOs wish to go”.

References and Notes

- (1) This laboratory is part of the Equipe de Recherches no. 549 associated with the CNRS.
- (2) To evaluate the energy E_a gained during a lifetime one can use the expression $k = A \exp(-E_a/RT)$. The preexponential factors A are 10^8 and 10^{13} s^{-1} for unimolecular and bimolecular processes, respectively. The rates k of fluorescence and phosphorescence (radiative processes with which the photoreaction must usually compete) are in the 10^8 – 10^9 and 10^0 – 10^3 s^{-1} ranges.
- (3) For a general discussion of avoided crossings see (a) L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975); (b) A. Devaquet, *Pure Appl. Chem.*, **41**, 455 (1975).
- (4) J. Michl, *Top. Curr. Chem.*, **46**, 1 (1974), in particular pp 51, 52.
- (5) D. Grimbert and L. Salem, *Chem. Phys. Lett.*, **43**, 435 (1976).
- (6) The potential energy curves reported in this article have been calculated in the following fashion: (a) The SCF part was carried out using the Gauss 70 program⁷ in its minimal basis set version;⁸ (b) The CI step includes all singly, doubly, and triply excited configurations constructed from the six highest occupied MOs (five in the case of the triple excitations) and the two lowest unoccupied. Note that the inclusion of the triply excited wave functions brings an average stabilization of the excited states of 2.4 kcal/mol (and a maximum of 4.5 kcal/mol).
- (7) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, No. 238, Indiana University, Bloomington, Ind.
- (8) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (9) (a) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974); (b) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).
- (10) The A and S character of the MOs or states refer to their antisymmetric or symmetric behavior with respect to the plane of the paper or, in other words, the plane of formaldehyde system. The D and Z states are schematized in the following way. The π_{CO} and π^*_{CO} orbitals which are mainly concentrated on the oxygen and carbon atoms of the carbonyl group have been completely localized on these centers (circles). The in-plane σ_{CH} bonding function is also shown linking the oxygen end and the hydrogen atom of the CH_2OH group.
- (11) In these calculations the O(carbonyl)–C(methane) distance is 2.60 Å (see ref 9a). This distance is kept constant while the hydrogen atom is gradually exchanged between methane and formaldehyde. The reaction coordinate is, for example, the CH distance. All other geometrical parameters were allowed to change by small increments proportional to the CH length changes from their initial to final values.
- (12) In this case the C(methane)–C(formaldehyde) separation remains constant but its value based on the carbon van der Waals radius (1.30 Å) is now 3.40 Å. The C(methane)–H distance is a convenient reaction coordinate which governs the linear variation of the other geometrical parameters between their initial and final values.
- (13) The oxygen atom of the alkoxy group bears two lone pairs. The first (n) is now antisymmetric (π) with respect to the plane of the paper and comes from the familiar carbonyl oxygen lone pair. Its counterpart (n') belongs to the plane of the paper (σ symmetry). These two orbitals should be degenerate when the two methyl and methoxy fragments are at infinite separation. This is not exactly so here because of residual interactions between n' and nearby methyl orbitals.
- (14) In both diagrams the S and A character refers to the symmetric or antisymmetric behavior of MOs or states with respect to the plane of the paper (to which the formaldehyde plane is now perpendicular). In the D and Z states of Figure 4b the oxygen n orbital is represented by a circle whereas half of the n' parent is schematized in the plane of the paper. The bonding orbital of the newly formed CH bond is also mentioned.
- (15) As pointed out by a referee this discussion would apply well to exchange reactions such as $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$. Indeed the best current estimate of the saddle point height in this (ground state) reaction is 9.5 kcal/mol.¹⁶ The narrow curving parabolic energy channel in this system results from the symmetry avoided crossing of two MOs, namely, the σ_{HH} bonding wave function of the H_2 molecule and the 1s atomic orbital of the hydrogen atom.¹⁷
- (16) D. G. Truhlar, *J. Am. Chem. Soc.*, **94**, 7584 (1972).
- (17) (a) W. A. Goddard III and R. C. Ladner, *J. Am. Chem. Soc.*, **93**, 6750 (1971); (b) V. Bonacic-Koutecky, J. Koutecky, and L. Salem, *ibid.*, **99**, 842 (1977).