QUANTUM MECHANICAL MODELS IN CATALYSIS

A.L. Tchougréeff[1]

Karpov Institute of Physical Chemistry, Moscow, Russia.

Abstract. We applied the general quantum mechanical ideas in order to establish the form of the many electron wave functions suitable for analysis of catalytic processes. This led us to the conclusion that the relevant wave functions for the electrons of the catalytic complexes must be taken as superpositions of the antisymmetrized products of the wave functions of electrons in excited and ionized states of the catalyst and reactants. With use of the trial wave function for the electrons of the catalytic complex in such a form it becomes possible to construct a model potential energy surfaces of catalytic reactions as a superposition of the potential energy surfaces of the reactants in different electronic states. We formulate the criteria which when satisfied make it possible to implement a catalytic version of a desired chemical transformation. We also propose an approach to explanation of the frequently observed correlations between the catalytic activity and other physical properties of a catalyst.

I. Introduction

The satisfactory theoretical description of the phenomenon of catalytic activity has not been evolved yet. Its obvious complexity makes it problematic that the progress of purely numerical quantum chemistry will give us a chance to predict the catalytic activity and to analyze related phenomena. Even when it happens a simple qualitative model of catalysis will be nevertheless necessary. In this paper we try to approach catalysis from a general point of view *ie.* to understand its qualitative features considering it as a quantum mechanical problem. This approach is not designed for immediate calculations of the catalytic reactions, but to provide a basis for such calculations and (which is more important) for analysis of frequently diverse experimental data related to catalysis.

II. Physicochemical preliminaries.

Let us consider a simple reaction:

[1]Present address: Max-Planck-Institut für Physik komplexer Systeme, Dresden, 01187, Germany

$$R \rightarrow P \tag{1}$$

transforming a reactant R to a product P. Let us assume that the reaction rate is described by the first order kinetic equation:

$$d[P]/dt = -d[R]/dt = k[R] \tag{2}$$

Obviously, the need in catalysis appears when the half transformation time $t_{1/2} = \ln 2/k$ is too long (the rate constant k is too small). Adding a catalyst C replaces the original first order reaction by the following chain of reactions:

$$R + C \rightleftarrows CR \rightarrow CP \rightleftarrows C + P \tag{3}$$

with the rate constants k_2 for the formation of CR from C and R; k_{-1} for the decomposition of CR into C and R; k_c for the intramolecular transformation of CR to CP(the catalytic step itself); k_1 for the decomposition of CP to C and P; and k_{-2} for the formation of CP from C and P. With the standard assumptions concerning the stationary concentrations of CR and CP:

$$d[CP]/dt = d[CR]/dt = 0$$

and with the reasonable hierarchy of the relative rates when the catalytic step is still the rate determining step (the constant k_c is smaller than all other constants) and with the equilibria in both the reversible stages shifted towards the free reactant (or product) and free catalyst (the decompositions are much faster than the formations) the rate equation for the kinetic mechanism Eq. (3) gets the form:

$$d[P]/dt = \frac{k_c k_2 [C]}{k_{-1}}[R] = k_{eff}[R] \tag{4}$$

The half transformation time $t^c_{1/2} = \ln 2/k_{eff}$ and the catalyst makes its job if $t^c_{1/2} << t_{1/2}$, or in other words $k_{eff} >> k$.

This result is for sure well known and rather obvious. The formal kinetics cannot give more than a simple conclusion that the effective rate constant in a catalytic process must be larger that the rate constant for the reaction of the free reactants. However, experiments on catalysis give more than that. They say that not only the effective rate constants are larger, but also that the measured activation energies of the catalytic processes are smaller than the activation energies of the transformations of the free reactants. To proceed further and accommodate these data let us assume the Arrhenius form for the temperature dependencies for all the involved rate constants:

$$\begin{aligned} k &= A\exp(-\Delta E^{\neq}/k_B T) \\ k_c &= A_c\exp(-\Delta E_c^{\neq}/k_B T) \\ k_{\mathit{eff}} &= A_{\mathit{eff}}\exp(-\Delta E_{\mathit{eff}}^{\neq}/k_B T) \end{aligned} \tag{5}$$

and the standard form for the equilibrium constant:

$$K = k_2/k_{-1} = \exp(-\Delta G/k_B T). \tag{6}$$

where all the energy differences are positive. The situation when a necessity in a catalyst arises can be reformulated here in terms of the activation energies. Namely, we need a catalyst when the activation energy for the noncatalytic transformation is too high and we expect from the catalyst that the effective activation barrier for the catalytic process $\Delta E_{\mathit{eff}}^{\neq}$ will be lower than the original barrier $\Delta E^{\neq}$. This gives us a condition for the activation energy of the catalytic step. Indeed, combining the above expressions Eqs. (4) - (6) we get:

$$\begin{aligned} k_{\mathit{eff}} &= A_c[C]\exp(-(\Delta E_c^{\neq} + \Delta G)/k_B T) \\ \Delta E_{\mathit{eff}}^{\neq} &= \Delta E_c^{\neq} + \Delta G \\ A_{\mathit{eff}} &= A_c[C] \end{aligned} \tag{7}$$

Now we can see that the activation energy of the transformation of CR to CP must be that small that the sum $\Delta E_c^{\neq} + \Delta G$ is smaller than the activation energy of the noncatalytic reaction $\Delta E^{\neq}$, *ie*:

$$\Delta E_c^{\neq} + \Delta G < \Delta E^{\neq}, \text{ or } \Delta E_c^{\neq} < \Delta E^{\neq} - \Delta G, \text{ or } \Delta G < \Delta E^{\neq} - \Delta E_c^{\neq}. \tag{8}$$

This result is also known. However, it allows us to make certain conclusions concerning the general nature of catalysis. We can say that catalysis is a "coarse" phenomenon, the effect of catalyst is not just a weak perturbation but by contrast, for it could manifest itself the energetic characteristics of the system must be changed that much that the difference between the perturbed and unperturbed activation energies becomes larger than a finite positive energy ΔG.

III. Quantum mechanical treatment.

Now the problem of catalysis is reformulated in terms of the activation energies and quantum chemistry may be applied. From the point of view of quantum chemistry the activation energies are related with the potential energy surfaces (PES) of the transforming molecular systems. The problem may be formulated as follows: How the PES of reactants is modified when they are coordinated to a catalyst? What parameters of the catalyst affect this modification?

Here a comment should be made. Strictly speaking two PES's - that of the free reagents and that for the catalytic complex cannot be compared since the sets of the nuclear coordinates for the two do not coincide. At the same time it seems reasonable that the nuclear coordinates of the catalyst itself do not vary significantly in the course of the $CR \to CP$ transformation by contrast to the nuclear coordinates of the coordinated reactants. We neglect the variation of the nuclear coordinates in the catalyst and will consider them as fixed in an appropriate configuration. Then the PES of the catalytic complex becomes a function of the nuclear coordinates of the reactants only.

The high activation energy of the noncatalytic transformation means that on the PES the reactant valley (R) and the product valley (P) are separated by a high energy barrier. The energetic profile (EP) of such a transformation drawn along a path going from one valley to another has the form shown on Fig. 1. Quantum mechanics gives the well known relation between the electronic structure of the reactants (products) and the PES of their mutual transformations [2]:

$$E_R^0(q) =< \Psi_R^0(q) \mid H_R(q) \mid \Psi_R^0(q) > \tag{9}$$

where $\Psi_R^0(q)$ is the wave function for the ground state of electrons of the reactants (products), $H_R(q)$ is the electronic Hamiltonian for the reactants, and q is the full set of the nuclear coordinates of the reactants. The wave function $\Psi_R^0(q)$ describes the electronic structure of the reactants (products) and $E_R^0(q)$ is nothing else rather than the PES to be found. Making the calculations of the electronic structure for different points along the transformation path we get also the EP and than easily find the energy barrier along the given path.

In the case of the catalytic reaction we are interested in the catalytic step *ie.* in the transformation of the CR complex into the CP complex. On the PES of these complexes there should be a valley of the coordinated reactants and that of the coordinated products. However, the energetic barrier separating these two valleys must be significantly lower than that for the free reactants and products (Fig. 2). As it was before the PES is directly related to the electronic structure described by the electronic ground state wave function:

$$E^0(q) = < \Psi^0(q) \mid H(q) \mid \Psi^0(q) >, \tag{10}$$

where $E^0(q)$ is the PES, $\Psi^0(q)$ is the ground state wave function of the electrons of the whole complex, and $H(q)$ is the Hamiltonian for the complex, having the form

$$H(q) = H_R(q) + H_C(q) + H_{int}(q), \tag{11}$$

where $H_C(q)$ is the Hamiltonian for the electrons in the catalyst, $H_{int}(q)$ is the interaction operator for the catalyst and the reactants.

At this point there is a possibility to employ some standard quantum chemical method in order to find the wave function $\Psi^0(q)$ for each configuration of the reactant nuclei q and by this to find $E^0(q)$. However, our main goal is to derive some qualitative rules for catalysis on the basis of quantum mechanics. For that reason we proceed further trying to find what is the relevant approximate form of the ground state wave function $\Psi^0(q)$.

We consider first the case when the catalyst and reactants do not interact *ie.* $H_{int}(q) = 0$. In this limit all the electronic states of the catalytic complexes are precisely the antisymmetrized products of the electronic eigenstates of the catalyst and reactants (or products) [2]. Let $\Phi^i_R(q)$ and Φ^k_C be the many electron wave functions (may be approximate) for the i-th eigenstate of the reactants (products) and for the k-th eigenstate of the catalyst. Then each state of the catalytic complex has the form:

$$\Phi^i_R(q) \wedge \Phi^k_C, \tag{12}$$

where $\wedge$ stands for the antisymmetrized product. The energies of these states are:

$$E_{ik}(q) =< \Phi^i_R(q) \wedge \Phi^k_C \mid H_R(q) + H_C \mid \Phi^i_R(q) \wedge \Phi^k_C >= E^i_R(q) + E^k_C$$

$$E^i_R(q) =< \Phi^i_R(q) \mid H_R(q) \mid \Phi^i_R(q) > \tag{13}$$

$$E^k_C =< \Phi^k_C \mid H_C \mid \Phi^k_C >$$

(we remind that the interaction between the catalyst and the reactants is zero for the moment). A possible picture of the crossections of the PES's for the several electronic states of the catalytic complex is shown in Fig. 3. The shapes of all curves $E_{ik}(q) = E^i_R(q) + E^k_C$ for a given i reproduce the shape of the i-th reactants' term; they are merely shifted by the energy of the k-th state of the catalyst. The curve in the very bottom of Fig. 3 repeats the shape of the unreactive ground state term of the reactants and has the same energetic barrier as the corresponding term of the free reactants (see Fig. 1). Other terms of the catalytic complex repeat the shapes of the corresponding reactant terms. Among the excited (or ionized) reactant states there may be reactive states which either have a low barrier separating the reactant valley form the product valley or do not have any barrier at all.

Turning the interaction on ($H_{int}(q) \neq 0$) results in that the product-states Eq. (12) introduced above are not any more the eigenstates of the catalytic complex. However they form a complete basis of the electronic states of the complex and the real ground state of the latter can be expanded over this basis [2]:

$$\Psi^0(q) = \sum_{i,k} A^0_{ik}(q) \Phi^i_R(q) \wedge \Phi^k_C, \tag{14}$$

$$\sum_{i,k} A^0_{ik}(q)^2 = 1.$$

The formula Eq. (14) is a well known expansion of the ground state wave function of a composite system over the products of the states of the component subsystems. In that respect there is nothing new in it. On the other hand it should be noted that none of the existing quantum chemical numerical programs employs such a form for the trial wave function.

Inserting now $\Psi^0(q)$ Eq. (14) in Eq. (9) for the PES of the catalytic complex and taking into account that the states $\Phi^i_R(q)$ and Φ^k_C are the eigenstates of the subsystem operators $H_R(q)$ and H_C, respectively, so that only the interaction operator $H_{int}(q)$ can mix the states having $i,k \neq i',k'$, we get:

$$
\begin{aligned}
E(q) = &< \Psi^0(q) \mid H(q) \mid \Psi^0(q) >= \\
&= \sum_{i,k} A^0_{ik}(q)^2 (E^i_R(q) + E^k_C) + \qquad (15) \\
+ \sum_{i,k} \sum_{i',k'} & A^0_{ik}(q) A^0_{i'k'}(q) < \Phi^i_R(q) \wedge \Phi^k_C \mid H_{int} \mid \Phi^{i'}_R(q) \wedge \Phi^{k'}_C >
\end{aligned}
$$

This expression serves as a basis for our further analysis. It provides an explicit form of the PES of the catalytic complex. Ley us consider first the sum over i and k in Eq. (15). It is an average of all the terms $E_{ik}(q) = E^i_R(q) + E^k_C$ with the weights $A^0_{ik}(q)^2$. By this way the i-th excited or ionized states of the reactants contribute to the PES of the ground state of the catalytic complex and modify the original PES of the unreactive ground state of the free reactants (Figs. 1, 3). Let us consider a crossection of the PES of the catalytic complex along a certain path going from the reactant valley to the product valley in the nuclear coordinate space. Since the PES of the ground (unreactive) state has the high energetic barrier between the valleys the EP along any of paths going from one valley to another has the shape shown in Fig. 1. (It should not be necessarily the real reaction path. For the real reaction path the height of the energetic barrier is the smallest possible and coincides with the activation energy but we do not require that in our reasoning). If there are some reactive (with respect to the transformation of R to P) states (excited or ionized) then on the corresponding PES's the barriers separating the reactants and the products are either low or vanish at all. In this case for some paths connecting the reactants with the products the picture of the energy profiles looks like that shown in Fig. 3. Let us consider one of such paths. The superposition of the EP's of the excited and ionized reactive states with the EP of the unreactive ground state will give the resulting EP of the ground state of the whole complex along the chosen path. Obviously the barrier on this EP will be lower than that on the ground state EP. The second sum in Eq. (15) acts in a way that the whole PES (EP) of the catalytic complex with interaction shifts to the lower energy as compared to the ground state term of the complex without interaction. Finally the picture of the energy profiles for the catalytic complex acquires the form presented in Fig. 4.

It is easy to see that we have got what we wanted from the PES of the catalytic complex: the energetic barrier on the path leading from the coordinated reactants to the coordinated products is lower than the barrier for the transformation of the free reagents along the same path (see Fig. 2 and 4).

Now we can formulate the conditions when such a barrier lowering could take place and also indicate the factors controlling the effectiveness of this lowering. It should be noted first of all that it cannot be guaranteed *a priori* that the reactive (barrierless) excited (or ionized) states exist. If they are absent we should admit that the rate of the process at hand cannot be increased by adding a catalyst. However, the opposite is also true: if some transformation impossible (or difficult to perform) in the ground state of the free reactants turns out to be feasible in a catalytic version, that means that there are reactive electronic states of the reactant, which were admixed to the unreactive ground state. Nothing else except the modification of the reactant PES under the influence of a catalyst can happen. And this modification is described by the coefficients $A^0_{ik}(q)$ in the expansion Eq. (14) of the wave function of the ground state of the complex. The larger by the absolute value are the coefficients of the reactive states the stronger the barrier lowers in the catalytic complex as compared to the free reactants. The coefficients can be estimated approximately:

$$A^0_{ik}(q) \propto \frac{< \Phi^i_R(q) \wedge \Phi^k_C \mid H_{int} \mid \Phi^0_R(q) \wedge \Phi^0_C >}{((E^i_R(q) - E^0_R(q)) + (E^k_C - E^0_C))} \tag{16}$$

Obviously, it is necessary for the barrier lowering that the matrix element of the interaction between the unreactive ground state of the complex and its reactive excited state standing in the numerator is not vanishing. This condition imposed on the interaction matrix element generates certain symmetry selection rules discussed in details in [3-6]. It is clear that the larger is the magnitude of the matrix element the larger also is the corresponding coefficient.

The denominator of Eq. (16) is nothing else than the sum of the excitation (or ionization) energies of the reactants and of the catalyst $\Delta E^i_R(q) = (E^i_R(q) - E^0_R(q))$ and $\Delta E^k_C = (E^k_C - E^0_C)$. It is easy to see that if the energy of the i-th reactive state of the reactants $\Delta E^i_R(q)$ is large as compared to the interaction matrix element the coefficients $A^0_{ik}(q)$ are small. Respectively, the extent of the modification of the PES will be also small as small will be the hope to perform the desired process with aid of a catalyst. Strictly speaking, there is no difference whether the reactive states do not exist at all or their energies are too high.

The second term in the denominator is the excitation energy of the catalyst. If the energy necessary to excite (ionize) the reactants to the i-th reactive state is not too high it is the energy of the k-th excited (ionic) state of the catalyst ΔE_C^k that actually controls the degree of the admixing of the reactive state and thus the extent of the modification of the PES. The lower is this energy the more effective the admixing is and the higher is the catalytic activity.

The last notion allows one to rationalize the correlations between the activity of catalysts and other physical properties of the latter. The correlations of that type are frequently reported in the literature on catalysis, but the reasons for these correlations to exist are never given and the whole picture remains quite confusing. In the framework of the present approach the correlations of that sort appear naturally: any physical measurement probing the excitation (ionization) energy ΔE_C^k must correlate with the catalytic activity when the k-th excited state of the catalyst dominates the modification of the PES according to Eqs. (15), (16). That can be g-factor, chemical shift, position of the absorption band in the electronic excitation spectrum and other properties (see [3-6] for details).

IV. Discussion.

The proposed approach to modelization of the modified PES's is useful first of all for the qualitative analysis of the catalytic activity. For the purposes of qualitative reasoning there is no need to calculate the PES, it is enough to construct a model PES. The input information for such a model can be obtained from various experimental sources. Photochemistry can provide the information on the PES's of the excited states, electron absorption spectroscopy or magnetic measurements can provide the information on the energies and the symmetries of the catalyst excited states.

Let us discuss briefly the relations between the proposed approach and the theoretical models of catalytic activity existing in the literature. The theoretical studies presenting a general description of this phenomenon are largely performed in the context of heterogeneous catalysis because of the the obvious industrial importance of the latter (for recent review see [7]). The "state-of-art" calculations address mainly homogeneous processes of specific interest (for review see [8,9]). However, the borderline between the two is very much conditional and the problems faced by quantum chemistry when it adresses the both are basically the same. As is has been mentioned in [10] the understanding of chemical reactivity is not possible without the knowledge of the reaction EP's which are to be calculated by quantum mechanical techniques. The problem which any theory of the catalytic action faces in this context is that such a theory must be able to compare the EP of the gas phase reaction of the free reactants with that of the adsorbed (in the case of heterogeneous catalysis) or coordinated (in the case of homogeneous catalysis) reactants. The difference between the EP's is given by the heat of chemisorption (or by the heat of formation of the catalytic complex) Q which in its turn depends on the reaction coordinate and must be larger for the transtion state of the gas phase reaction than for the equilibrium configuration of the reactants. However, the heats of chemisorption are known from the available quantum chemical calculations with very low accuracy and are subject to irregular variations depending on adsorption site, geometry, *etc.* [10]. The reason of this failure lay obviously in the fact that both the theories and numerical schemes applied to the electronic structure of the catalytic complexes all use the single determinant SCF-MO-LCAO approximation as their basis [7-9]. It is known, however, that the MO-LCAO approximation has very poor performance when applied to the problem of bond formation. The reason for this in its turn is the well known deficiency of the SCF-MO-LCAO trial wave functions which overestimate the contribution of the configurations with electrons transferred between the parts of the system (the charge transfer configurations) as compared to their real contribution to the exact ground state wave function. This defect is very difficult to correct and very long CI expansions are needed to achieve a reasonable description if the canonical MO's spread over the entire system are used as an one-electron basis to construct the many electron configurations. For the numerical calculations on the energetics of chemisorption (or complex formation) when the system under consideration is large enough the effects of the CI truncation are difficult to assess and to control. This shortcoming becomes particularly unpleasant when the methods based on the SCF-MO-LCAO approximation address the complex formation or chemisorption in the context of catalysis. We mentioned already that in a successful catalyst both the reactants and products are relatively weakly bound and thus the error introduced by the SCF-MO-LCAO approximation when applied to such a system is particularly large.

In order to avoid these problems it is necessary to use a trial wave function which (i) would have the correct behaviour at the large separation between the reactants (products) and the catalyst; and (ii) would be able to describe weak covalent bonding between the fragments. The property (i) is clearly satisfied by the group (or generalized product) wave functions [11]. This approach is proved to be extremely successful. It is enough to say that the famous $\sigma - \pi-$separation was substantiated within this approach [12]. The group function approach differs fundamentally from the MO-LCAO picture by developping the states of a composite system in terms of the states of its fragments [13,14]. However, this approximation as it is formulated, for example, in [11] implies that the number of electrons on each of the fragments remains fixed. That prevents from satisfying the condition (ii) *i.e.* from describing the covalency since the latter appears due to the electron transfers between the fragments. A way out has been proposed in [3-5,14-16] where the standard group function expansion [11] has been supplemented by the configurations with one electron transferred from one fragment to another. It has been shown in [14] that this type of the trial function covers the both limits - that of the separated fragments and that of the covalenly bonded ones. Apparently, this type of the function satisfies the conditions (i), (ii).

The approach presented above has been earlier applied to the catalytic isomerization of quadricyclane to norbornadiene in the presence of the metal-porphyrins as catalysts [3-5]. This reaction is a classical example of a reaction restricted by the Woodward - Hoffmann symmetry rules. The catalytic activity in this reaction must correlate with the energy of the first excited state having the total spin different by one from that of the ground state of the catalyst. This prediction has been verified for a series of the metal porphyrins [5]. It has been found that only the complexes with the relatively low energy of the first excited state (those of Co^{2+}, Fe^{2+}, and Co^{3+}) are catalytically active in this reaction. By contrast the complexes where the first excited state of the necessary spin has higher energy are not active (Mn^{2+} and Fe^{3+}). The wave functions of the same form were succesfully used in [15,16] in order to analyze qualitatively some other cases of the catalytic activity.

In this paper we present a carcass of a theory of the catalytic action based on the trial wave function Eq. (14) [3,14,15] satisfying the conditions (i), (ii) rather than on a SCF-MO-LCAO wave function. It turns out that even on a qualitative level the new trial function is useful since it allows one to construct model EP's for the catalytic reactions under very general assumptions. In certain extent the proposed approach fills the gap between the phenomenological thermodynamic approach to catalysis presented in [10] and the demand for the quantum mechanical description of the EP formulated in the same work. The present approach is still on the phenomenological side, but it operates with the microscopic quantum parameters of catalysts and reagents, namely with their excitation (or ionization) energies, rather than with the thermodynamical ones, like binding energies. The parameters involved in the present scheme are well defined and at least in principle observable, so that the requirement for a working alternative to a complete numerical simulation of the real catalytic complexes on the quantum chemical level to use only observable parameters formulated in [10] is also satisfied. The attractive capacity of the present method to rationalize the correlations between the catalytic activity and various physical properties of the catalysts has been already mentioned above.

Our conclusion that the ionization and excitation energies of the catalysts must be reliable indices of their catalytic activity has been suspected by many authors (for review see [7]). However, as far as we know, the statements of that type have never been a result of a sequential derivation with some clearly formulated general assumptions. If a single determinant (SCF) trial wave function is used in order to describe the catalytic complex that restricts the catalysts can be described to the metal surfaces only and makes it hardly possible to describe any transformation of the reactants since the correlation effects are well known to be important in the vicinity of the barrier top. When the catalyst-reactant interactions are addressed within the SCF approximation the contribution of the charge transfer states is overestimated. For that reason the rôle of the catalyst ionization energies (*i.e.* of the Fermi energy and of everything which is related to the latter) as the indices of the catalytic activity is probably overstressed. The ionization energies are very probable activity indices in the case of catalysis by metal surfaces and clusters. However, in the case of catalysis by the paramagnetic transition metal complexes the excited rather than ionized states of both the catalyst and reactants give the leading contribution to the ground state Eq.(14) of the catalytic complex [3-6]. Respectively, the excitation rather than ionization energies of the paramagnetic complexes are the relevant indices of their catalytic activity. In the domain of heterogeneous catalysis the excitation energies will be important indices of the activity of paramagnetic transition metal oxides and of other insulators with localized d-electrons. In that case the SCF approximation apparently does not apply to the separate catalyst either.

On the quantitative level a consistent numerical scheme for calculations of the EP's of the catalytic reactions implementing the trial wave function Eq. (14) is still to be developed. The respective code must be capable to cover rather large systems so many technical tricks are to be invented. This work is in progress now.

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Figure Captions

Fig. 1. A crossection of the PES (energy profile) of a kinetically hindered reaction of the free reactants along a path in the nuclear coordinate space of the reactants (products).

Fig. 2. A crossection of the PES of a transformation of the catalytic complex along the path connecting the valleys of the coordinated reactants and products. Only the nuclear coordinates of the reactants are allowed to vary, the nuclear coordinates of the catalyst are frozen.

Fig. 3. The energy profiles for the basis states of the catalytic complex (the interaction between the catalyst and the reactants is turned off).

Fig. 4. The energy profiles of the basis states of the catalytic complex and of their superposition corresponding to the ground state of the catalytic complex with the turned on interaction.

Fig. 5. The results of the application of the method of this paper to the catalytic isomerization of quadricyclane to norbornadiene. Dashed lines present the ES's obtained with use of the single determinant wave functions for the reactant and the product respectively. The solid lines present the result of the $3 \times 3CI$ calculation for the unreactive ground state and for the reactive excited state. The dotted line is the result of the superposition of the reactive and unreactive states of the reactants according to Eq. (15).

In the one-determinant approximation applied to the four electrons occupying the four π-orbitals of the norbornadiene the energy profiles for the reactant and product Slater determinants intersect as it is shown in Fig. 5. This intersection is the result of the intersection of the occupied and empty orbitals of the different symmetry occuring in some point on the reaction path. When the configuration interaction is turned on the EP for the $^1A_1$ ground state becomes smooth and the estimate for the barrier is more realistic [3]. Moreover the simplest $3 \times 3CI$ applied to the system of four electrons in four orbitals gives the EP for a triplet excited $^3A_2$ state as well. From the picture of the EP's it is clear that the $^1A_1$ ground state is the unreactive state and the $^3A_2$ state is the reactive one. The latter fact is also known from photochemistry since the reverse reaction - that of formation of quadricyclane from norbornadiene proceeds under the light irradiation in the presence of a triplet sensitizer.