

Physical Chemistry

Quantum mechanical models in catalysis

A. L. Tchougréeff

*L. Ya. Karpov Institute of Physical Chemistry,
10 Vorontsovo pole, 103064 Moscow, Russian Federation.
Fax: +7 (095) 975 2450. E-mail: andrei@cc.nifhi.ac.ru*

A wave function of electrons of a catalytic complex taken as a series of products of wave functions of the reactants and catalyst was suggested for use in modeling potential energy surfaces of catalytic reactions and for analysis of catalytic activity. Quantum mechanical criteria at which catalytic transformations become possible were formulated on the basis of this concept. The character of correlations between the activity and physical properties of catalysts was explained, and a general procedure for theoretical analysis of such correlations was described.

Key words: theory of catalysis, model potential energy surfaces, quantum mechanics.

Presently, the problem of theoretical description of catalytic activity is far from solution. Its evident complicated character does not allow one to expect that purely computational methods of quantum chemistry are able to consistently describe catalytic activity and explain its relationship with other properties of molecules in the foreseeable future. Therefore, it is of interest to study the phenomenon of catalysis by qualitative methods and to consider it as a quantum mechanical problem. This approach is not aimed at numerical calculation of all values related to catalysis, but it helps to use various (often unrelated to the problem at first glance) experimental facts in analysis of catalytic activity. It also makes it possible to analyze and explain the known examples in which the activity of catalysts enigmatically correlates with their physical properties. In addition, as will be shown, the approach suggested allows one to expect the development of computational quantum chemical methods that would efficiently serve to describe the phenomenon of catalysis.

In a very general form, the quantum mechanical interpretation of the catalytic activity can be reduced to comparison of two potential energy surfaces (PES), namely: the PES of rearrangement of free reactants to free products and the PES of the same rearrangement, when both reactants and products are components of the catalytic complex. It is noteworthy that these two PES cannot formally be compared, because the sets of nuclear coordinates do not coincide for the free reactants/products and the catalytic complex. At the same time, it seems reasonable to assume that the coordinates of nuclei of the catalyst change insignificantly upon rearrangement of the coordinated reactants to coordinated products, unlike the coordinates of nuclei of the reactants/products.

We neglect changes in the coordinates of the catalyst nuclei and consider PES as a function of coordinates of the reactants only, considering the catalyst coordinates "frozen" in some appropriate configuration. Taking into account these assumptions, both PES become the func-

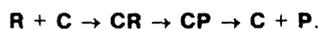
tions of the same set of nuclei coordinates, and the PES of the catalytic complex can be considered as the result of modification of the PES of free reactants/products due to their interactions with the catalyst. Of course, the routes of rearrangement of free reactants and reactants in the catalytic complex can strongly differ.

At the restriction mentioned, deformations of PES of reactants/products can be related to properties of the free catalyst. Let us consider the reaction $R \rightarrow P$, which transforms reactants R to products P . The PES of this transformation $E_R^0(q)$ is given by the expression¹

$$E_R^0(q) = \langle \Psi_R^0(q) | H_R(q) | \Psi_R^0(q) \rangle, \quad (1)$$

where $\Psi_R^0(q)$ is the wave function of the ground state of electrons of the reactants/products, $H_R(q)$ is the Hamiltonian for the reactants, and q is the full set of coordinates of nuclei of the reactants/products. Let us suppose that on PES of free molecules the valleys of the reactants (R) and products (P) are separated by a high energy barrier. The energy profile for such a reaction along any route from the valley of the reactants to the valley of the products has the form presented in Fig. 1.

The mechanism of the reaction involving catalyst C can simply be presented by the scheme²



Here we are interested in the rearrangement of the intermediate complex of the catalyst with the reactants (CR) into its complex with the products (CP). The

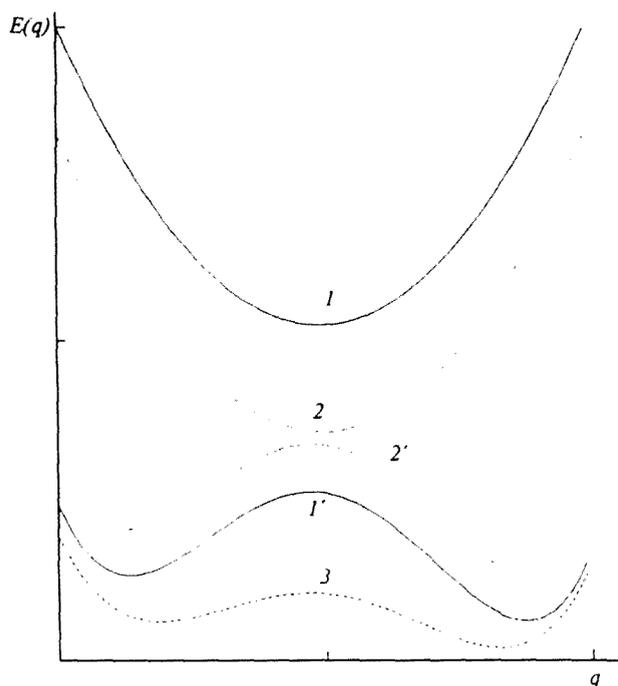


Fig. 1. Energy profiles of rearrangement for various electronic states of free reactants ($1, 1'$) and profiles of $E_{ik}(q)$ (Eq. (5)) for functions (Eq. (4)) ($2, 2'$) as well as the superposition of these profiles corresponding to the ground state of the catalytic complex (3).

valleys of the coordinated reactant and product should exist on the PES of the catalytic complex, and the catalysis will be efficient only if the energy barrier separating these two valleys is considerably lower than that in the case of the free reactant and product. As previously, the PES of the catalytic complex $E^0(q)$ is controlled by its electronic structure:

$$E^0(q) = \langle \Psi^0(q) | H(q) | \Psi^0(q) \rangle, \quad (2)$$

where $\Psi^0(q)$ is the wave function of electrons of the complex and $H(q)$ is its full Hamiltonian. The latter has the form

$$H(q) = H_R(q) + H_C(q) + H_{int}(q), \quad (3)$$

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

Let us consider the case when $H_{int}(q) = 0$ (separated reactants/products and catalyst). Then electronic eigenfunctions of the catalytic complex are exactly antisymmetrized products of electronic eigenfunctions of the catalyst and reactants/products¹:

$$\Phi_R^i(q) \wedge \Phi_C^k, \quad (4)$$

where the symbol \wedge stands for the antisymmetrized product and $\Phi_R^i(q)$ and Φ_C^k are the wave eigenfunctions of the i th state of electrons of the reactants/products and the k th state of electrons of the catalyst. The energies of these states are given by the expression

$$E_{ik}(q) = \langle \Phi_R^i(q) \wedge \Phi_C^k | H_R(q) + H_C | \Phi_R^i(q) \wedge \Phi_C^k \rangle = E_R^i(q) + E_C^k, \quad (5)$$

$$(E_R^i(q) = \langle \Phi_R^i(q) | H_R(q) | \Phi_R^i(q) \rangle, E_C^k = \langle \Phi_C^k | H_C | \Phi_C^k \rangle).$$

Any term $E_{ik}(q)$ has the shape of the i th term of the free reactants/products and is only shifted by the value of the energy of the k th state of the free catalyst E_C^k . Curve $2'$ in Fig. 1 repeats the form of the term of the unreactive ground state of reactants with its intrinsic barrier. Of excited (or ionized) states of the reactants, there are such states for which the energy barrier separating the valleys of the reactants and products is low or completely absent (reactive states).

Switching on the interaction ($H_{int}(q) \neq 0$) results in the situation when antisymmetrized products (4) are not eigenfunctions of the catalytic complex any more; however, the function of its ground state can always be presented as a linear combination of these products¹:

$$\Psi^0(q) = \sum_{i,k} A_{ik}^0(q) \Phi_R^i(q) \wedge \Phi_C^k, \quad (6)$$

$$\sum_{i,k} A_{ik}^0(q)^2 = 1; i, k = 0, 1, 2, \dots$$

Inserting $\Psi^0(q)$ into Eq. (2) and taking into account that $\Phi_{\mathbf{R}}^i(q)$ and $\Phi_{\mathbf{C}}^k$ are the eigenfunctions of operators $H_{\mathbf{R}}(q)$ and $H_{\mathbf{C}}$, respectively (thus, only operator $H_{\text{int}}(q)$ can mix the basis product functions with $i, k \neq i', k'$), we obtain the expression for the PES of the catalytic complex:

$$E(q) = \langle \Psi^0(q) | H(q) | \Psi^0(q) \rangle = \\ = \sum_{i,k} A_{ik}^0(q)^2 (E_{\mathbf{R}}^i(q) + E_{\mathbf{C}}^k) + \\ + \sum_{i,k} \sum_{i',k'} A_{ik}^0(q) A_{i'k'}^0(q) \langle \Phi_{\mathbf{R}}^i(q) \wedge \Phi_{\mathbf{C}}^k | H_{\text{int}} | \Phi_{\mathbf{R}}^{i'}(q) \wedge \Phi_{\mathbf{C}}^{k'} \rangle. \quad (7)$$

Formula (7) is convenient for analysis of qualitative features of PES of catalytic complexes; in particular, the first sum in it is the mean value of all terms $E_{ik}(q)$ in Eq. (5) with weight factors $A_{ik}^0(q)^2$.

Let us consider the PES cross section along some path in the space of nuclei coordinates, which connect the areas of coordinated reactants and products. This path may not coincide with the route of the noncatalytic reaction of the free reactants. Since the barrier between the valleys of the reactants and products of the PES of the ground (unreactive) state of the reactants exists, the energy profile along any path connecting these valleys has a barrier as well, and its height (activation energy) is minimum for the true reaction route.

If reactive (excited or ionized) states of reactants exist, the barriers on the corresponding PES, which separate the valleys of reactants and products, are either low or completely absent. Superposition (7) of the energy profiles of the excited (ionized) and ground states of reactants presented in Fig. 1 results in a lower barrier for the ground state of the catalytic complex along the path chosen than that of the unreactive ground state of reactants along the same path. Due to the second sum (with $i, k \neq i', k'$) in Eq. (7), the whole PES of the catalytic complex (Fig. 1, curve 3) will be lower than that of the ground state of the complex without interaction.

Now we can formulate the conditions of lowering the energy barrier and indicate the factors favoring it. First of all let us mention that the existence of reactive excited (ionized) states of reactants/products cannot be *a priori* ensured. If they are absent, this process cannot be catalyzed. On the contrary, if some transformation, which is not feasible or hardly performed for the ground state of free reactants, is performed catalytically, this indicates that some reactive electronic states of reactants exist and are admixed to their unreactive ground state.

Contributions of various basis states to the ground state of the complex are given by coefficients $A_{ik}^0(q)$ in series (6) and can be approximately estimated:

$$A_{ik}^0(q) \propto \frac{\langle \Phi_{\mathbf{R}}^i(q) \wedge \Phi_{\mathbf{C}}^k | H_{\text{int}} | \Phi_{\mathbf{R}}^0(q) \wedge \Phi_{\mathbf{C}}^0 \rangle}{(E_{\mathbf{R}}^i(q) - E_{\mathbf{R}}^0(q)) + (E_{\mathbf{C}}^k - E_{\mathbf{C}}^0)}. \quad (8)$$

The higher the absolute values of these coefficients for reactive states, the stronger the decrease in the barrier. In order to modify PES (to decrease the barrier),

it is necessary that the matrix element (in the numerator of Eq. (8)) of the operator of interaction between the functions of unreactive state $\Phi_{\mathbf{R}}^0(q) \wedge \Phi_{\mathbf{C}}^0$ of the complex and its excited state $\Phi_{\mathbf{R}}^i(q) \wedge \Phi_{\mathbf{C}}^k$ is not vanishing. This condition gives rise to symmetry selection rules, which we will not discuss in this work (see Refs. 3–8).

The denominator of Eq. (8) is the sum of excitation energies of the reactants ($\Delta E_{\mathbf{R}}^i(q) = E_{\mathbf{R}}^i(q) - E_{\mathbf{R}}^0(q)$) and catalyst ($\Delta E_{\mathbf{C}}^k = E_{\mathbf{C}}^k - E_{\mathbf{C}}^0$). When the energy of the i th reactive state of the reactants ($\Delta E_{\mathbf{R}}^i(q)$) is high, coefficients $A_{ik}^0(q)$ and, hence, the extent of deformation of the PES are low. (When the catalytic effect is absent, it is of no significance whether reactive states of reactants are absent *per se* or their energy is too high.)

When energy $\Delta E_{\mathbf{R}}^i$ of excitation of the reactants to some (i th) reactive state is low, summand $\Delta E_{\mathbf{C}}^k$ (for which the matrix element in the nominator of Eq. (8) is sufficiently high) controls the weight of the reactive basis state ($\Phi_{\mathbf{R}}^i(q) \wedge \Phi_{\mathbf{C}}^k$) in the ground state of the complex (6). This allows one to explain correlations between various physical properties of catalysts and their activity. Although the experimental works on catalysis report rather often about correlations of this sort, the reasons for their existence are not discussed, as a rule, and remain rather intriguing. It is quite evident in terms of our approach that any physical property, which is directly or indirectly related to the excitation energy $\Delta E_{\mathbf{C}}^k$, should correlate with the catalytic activity. This property can be the g -factor, chemical shift, positions of bands in electronic absorption spectra, *etc.*

This approach makes it possible to assign a more clear meaning to the usually uncertain term of "activation," which is often used in description of the catalysis phenomenon. According to Eqs. (6) and (7), the catalyst activates reactant molecules, admixing their reactive (barrierless) states to the unreactive ground state. Partial population of the reactive states upon interaction of the reactants and catalyst has a pure quantum mechanical character and cannot be observed for free molecules by any physical methods. In our approach, the activation does not coincide with the accelerated generation of an active (excited or ionized) free form of the reactant or with the thermal population of reactive states, which is often kept in mind when one speaks about the catalytic activation.

In this work, the PES of the catalytic complex is described in terms of PES and wave functions of its components, *i.e.*, free reactants and catalyst. Qualitative consideration of the catalytic activity does not require calculations of all states of reactants and catalyst, because information about excited states of reactants can be provided by the photochemistry and that about states of the catalyst can be obtained by various spectral methods. The model PES of the catalytic complex can be obtained using these as input data for analysis by the scheme proposed.

This approach to the problem of catalysis (or reactivity of organometallic compounds) was successfully used,

for example, for the catalytic isomerization of quadricyclane to norbornadiene in the presence of metalloporphyrins³⁻⁵; insertion of carbon monoxide into the metal-aryl bond in palladium, platinum, nickel, and cobalt complexes^{6,7}; and monooxygenation of organic substrates by oxene complexes of metalloporphyrins.¹⁰ In all the cases mentioned, the roles of reactants and catalysts were compared, and the reasons for the difficulty or impossibility of the reaction of free reactants yielding desired products were explained. The reactive states of free reactants and the states of catalysts with corresponding symmetry, which ensure admixing of reactive states with unreactive ones, were revealed. In all cases, comparison³⁻⁸ of different physical quantities related to energies of the catalyst states controlling its activity confirmed that the activity correlates with these quantities. This indicates that our scheme is valid and can be applied to analysis of various catalytic processes.

Now let us discuss the relation between the representation of the wave function of catalytic complex (6) proposed in this work and more traditional approaches of quantum chemistry. It should be noted that modern quantum chemistry is based on the Hartree-Fock (self-consistent field (SCF)) approximation, which presents the wave function of any system by one Slater determinant composed of its occupied molecular orbitals. It is known⁹ that when the interaction of subsystems is weak, this wave function does not flow to the limit corresponding to their isolated states.

In fact, at $H_{\text{int}} \cong 0$ (almost free catalyst and reactants/products) for the ground state of the catalytic complex, $\Psi^0(q) \cong \Phi_{\text{R}}^0(q) \wedge \Phi_{\text{C}}^0$. However, this limit cannot be obtained in the SCF approximation, which overestimates mixing of orbitals of separated subsystems and the contribution of charge-transfer configurations. This overestimation, which is sometimes denoted by the term "strong charge fluctuations," is the well known main defect of all one-determinant quantum chemical methods.

To correct this fault of the SCF scheme, several determinants corresponding to excited configurations are usually added to the Slater determinant of the ground state. This allows one to take into account correlation effects and suppress nonphysical charge fluctuations. However, the problem remains that the series of configurational interaction (CI) in the basis of multi-electron functions composed of mono-electronic MO of the SCF method converge very slowly. Many configurations are needed for satisfactory description. In this case, computational difficulties (large dimensionality of the CI basis) are aggravated by the impossibility to qualitatively analyze the PES of the process on the basis of the behavior of the small number of leading terms of the series. Use of wave function (6) as a trial one for the catalytic complex solves to some extent this problem.

Since the "correct" behavior of the trial wave function in the weak interaction limit is ensured by the special selection of the basis configurations, which sup-

press charge fluctuations, one can expect that series (6) will converge more rapidly than the usual CI series. A better convergence will allow one to restrict the expansion by shorter CI series and, hence, calculations of PES of catalytic complexes will be more available. In addition, trial wave function (6) assumes the physically clear analysis of the behavior of the catalytic complex in the framework of its components, using several leading series terms.

As an example of application of the approach proposed to analysis of the most general regularities of catalysis, we consider the known resemblance of the behavior of molecules coordinated (or adsorbed) on the catalyst and their free but ionized or excited forms. The authors of earlier works (see review¹⁰) tried to use this resemblance for substantiation of calculations of the "catalytic" reactions without explicit account of the catalyst. These calculations considered only transforming ligands (in the corresponding ionic states). Of course, this is a very rough approximation, because the extent of the resemblance mentioned could not be estimated and the possibility of presentation of the ligand as its free ionized form was not justified by the subsequent analysis of the electronic structure of the catalytic complex.

Moreover, this possibility cannot be justified in terms of the SCF approximation: in the one-determinant wave function of the catalytic complex, any individual character of its components is lost, and one can only speak conditionally about their certain states. Relative weights of individual states of the reactants and catalyst are strongly distorted by the SCF approximation, and the loss of their individual characters is an artefact of the SCF method rather than a reflection of the reality.

The mentioned overestimation of the electron transfer between subsystems by the SCF approximation results in both an incorrect wave function upon their weak interaction and smearing (strong fluctuations) of their individual states. On the contrary, wave function (6) of the complex establishes the measure of resemblance of the coordinated reactant to its ionized or excited form. Formula (7) presents the PES of the rearrangement of coordinated reactants to products as a superposition of PES of the ground and several excited and ionized states of free reactants instead of the rough substitution of the PES of the catalytic complex for the PES of the ionized or excited free ligand (as it was done previously¹⁰).

Now let us discuss the relations between the approach proposed and some available concepts of the quantum theory of catalysis. The vibronic theory of catalysis (activation) based on the semiquantitative analysis of contributions of different states of ligands to the ground state of the complex performed in the SCF approximation was suggested in Refs. 11 and 12 (see also monograph¹³ and works cited therein). The remarks on the limitations of the SCF scheme apply in full measure to this theory, because all theoretical conclusions¹¹⁻¹³ drawn in the framework of this theory are performed for the one-determinant wave function of

both the whole catalytic complex and reactants/products. Only in this case, vibronic and force constants of reactants can be presented as sums of the corresponding orbital constants multiplied by populations of the orbitals.

Changes in the orbital populations of the reactants upon their interaction with the catalyst results in damping and deformation of their vibrational modes, and, hence, the activation barrier of their rearrangement to the products decreases. According to the theory,¹¹⁻¹³ the changes in the orbital populations should be determined from the calculation of the catalytic complex; however, these key parameters remain unknown due to the basic difficulties of the SCF approximation that overestimates such changes and to arbitrary determination of orbital populations of a molecule in the complex. Therefore, in the subsequent development of the theory,¹³ orbital populations (sole parameters of the electronic structure in this theory) were excluded, and the expected changes in the activation energy were expressed by the observed changes in geometry and vibrational frequencies of the coordinated reactant. Thus, the vibronic approach rejects an attempt to establish the relationship between the electronic structure of the catalyst and its activity, which, in our opinion, should be the final purpose of the quantum theory of catalysis.

Substantiation of the vibronic approach to the catalysis seems doubtful, because the SCF approximation is *a fortiori* inappropriate for description of chemical transformations accompanied by cleavage and formation of bonds. The electronic wave function of the molecular system near the transition state of this reaction cannot be presented by one determinant (see, e.g., Refs. 3-5 and works cited therein). Therefore, potential curves with minima corresponding to reactants and barriers separating reactants and products, which are parametrized in terms of the vibronic approach, can be unrealistic. In contrast to this, our formalism does not require the SCF approximation for the wave function of the reactant and their representation as a cubic polynomial (one more assumption that is substantial for the vibronic approach). However, if the assumptions used for development of the vibronic theory of activation are accepted, its formulas can be obtained from the general expression (7).*

The approach described in this work generalizes and modifies wave function (9) suggested by K. Fukui¹⁴ for analysis of the interaction of molecules **A** and **B** in the presence of catalyst **C** ($\mathbf{A} + \mathbf{B} \xrightarrow{\mathbf{C}} \mathbf{AB}$), which has the form

$$\Psi^0 = \sum_{ijk} A_{ijk}^0 \Phi_A^i \wedge \Phi_B^j \wedge \Phi_C^k \quad (9)$$

Each of functions Φ_A^i , Φ_B^j , and Φ_C^k is either the corresponding Slater determinant of the free ground state or

the determinant composed of the same MO and corresponding to the transfer of one electron from (to) **A** or **B** and not more than two-electron transfer from (to) **C**. It is evident that Eq. (9) is a particular case of series (6), which assumes both ionized and excited states of the reactants/products and catalyst. In addition, the function of the ground state of the catalyst in Eq. (6) need not be one-determinant as in Eq. (9). The latter restriction strongly narrows the possibilities of application of wave function (9) for studying metal-complex catalysis, because ground states of transition metal complexes are often described incorrectly in the SCF approximation.¹⁵

At the same time, it was shown in terms of our approach^{6,7} that in several cases for series (6) one can use only products of functions of ionized states of free components of the catalytic complex. In these cases, the physical properties correlating with the catalytic activity are usually related to the orbital energies (more exactly, to the ionization potential and electron affinity) of the catalyst. However, in the case of paramagnetic metal complexes, catalytic activities correlate with energies of their d-d-excitations,^{3-5,8} and, hence, the products of the functions of excited states of the catalyst and reactants should certainly be included in the expansion. Only analysis using trial function (6) allows one to relate the activity of such a catalyst to the directly observed energies of its d-d-excited states rather than to the poorly determined energies of its HOMO and LUMO.¹⁴

Above never used (*cf.* Eqs. (3)-(8)) the assumptions that the catalyst is an isolated molecule. Therefore, the approach suggested can be equally applied both to homogeneous and heterogeneous catalysis. In the case when the catalyst is the crystal surface, the results of this work are generalized at once.

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