Quantum Mechanical Models in Catalysis

A. L. TCHOUGRÉEFF

Karpov Institute of Physical Chemistry, Moscow, Russia

ABSTRACT

We applied 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 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 the explanation of the frequently observed correlations between the catalytic activity and other physical properties of a catalyst. © 1996 John Wiley & Sons, Inc.

Introduction

A satisfactory theoretical description of the phenomenon of catalytic activity has not yet been evolved. Its obvious complexity makes it problematic in 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 nevertheless be necessary. In this article, we try to approach catalysis from a general point of view, i.e., 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.

Physicochemical Preliminaries [1]

Let us consider a simple reaction:

$$R \rightarrow P, \qquad (1)$$

transforming a reactant R to a product P. Let us assume that the reaction rate is described by the

first-order kinetic equation

$$d[P]/dt = -d[R]/dt = k[R]. \qquad (2)$$

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:

$$R + C \rightleftarrows CR \to CP \rightleftarrows C + P, \qquad (3)$$
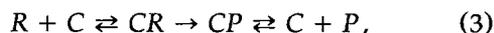
with the rate constants k_2 for the formation of CR from C and R; k_{-1} for the decomposition of CR into C and R; k_c for the intramolecular transformation of CR to CP (the catalytic step itself); k_1 for the decomposition of CP to C and P; and k_{-2} for the formation of CP from C and P. With the standard 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 reversible stages shifted toward 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

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

The half-transformation time $t_{1/2}^c = \ln 2/k_{eff}$ and the catalyst does its job if $t_{1/2}^c \ll t_{1/2}$, or in other words $k_{eff} \gg k$.

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 than the rate constant for the reaction of the free reactants. However, experiments on catalysis give more than that. They say that not only are the effective rate constants larger, but also that the measured activation energies of the catalytic processes are smaller than are 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 de-

pendencies for all the involved rate constants:

$$k = A \exp(-\Delta E^{\neq}/k_B T)$$

$$k_c = A_c \exp(-\Delta E_c^{\neq}/k_B T)$$

$$k_{eff} = A_{eff} \exp(-\Delta E_{eff}^{\neq}/k_B T), \qquad (5)$$

and the standard form for the equilibrium constant:

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

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 $\Delta E_{eff}^{\neq}$ will be lower than is 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

$$k_{eff} = A_c[C] \exp(-(\Delta E_c^{\neq} + \Delta G)/k_B T)$$

$$\Delta E_{eff}^{\neq} = \Delta E_c^{\neq} + \Delta G$$

$$A_{eff} = A_c[C]. \qquad (7)$$

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

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

$$\text{or } \Delta G < \Delta E^{\neq} - \Delta E_c^{\neq}. \qquad (8)$$

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 the catalyst is not just a weak perturbation, but, by contrast, as it could manifest itself, the energetic characteristics of the system must be changed so much that the difference between the perturbed and unperturbed activation energies becomes larger than a finite positive energy ΔG.

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 to the potential energy surfaces (PES) of the transforming molecular systems. The problem may be formulated as follows: How is the PES of reactants 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 $CR \rightarrow CP$ 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 in Figure 1. Quantum mechanics gives the well-known relation between the electronic structure of the reactants (products) and the PES of their mutual transformation [2]:

$$E_R^0(q) = \langle \Psi_R^0(q)|H_R(q)|\Psi_R^0(q)\rangle, \qquad (9)$$

where $\Psi_R^0(q)$ is the wave function for the ground state of electrons of the reactants (products); $H_R(q)$, the electronic Hamiltonian for the reactants; and q, 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 then easily find the energy barrier along the given path.

In the case of the catalytic reaction, we are interested in the catalytic step, i.e., 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
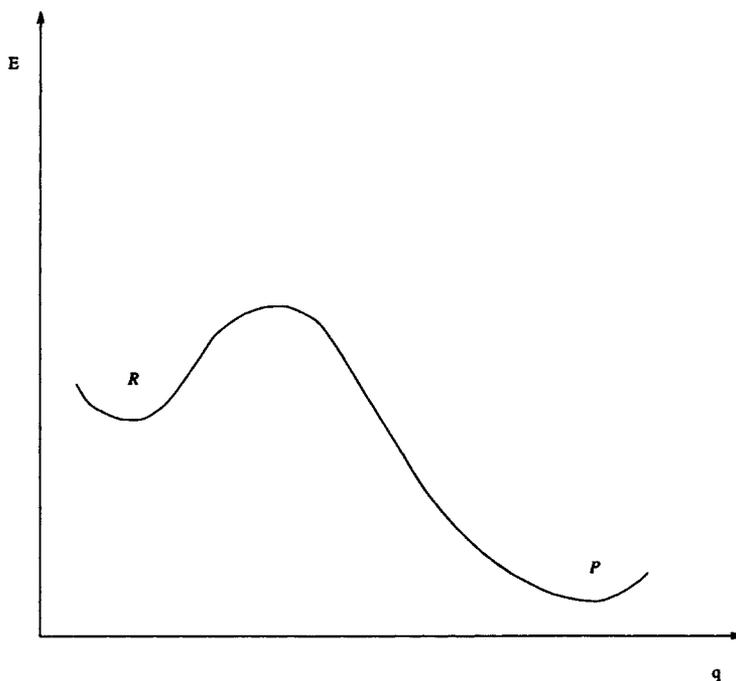
FIGURE 1. A cross-section of the PES (energy profile) of a kinetically hindered reaction of the free reactants along a path in the nuclear coordinate space of the reactants (products).

products (Fig. 2). As before, the PES is directly related to the electronic structure described by the electronic ground-state wave function:

$$E^0(q) = \langle \Psi^0(q)|H(q)|\Psi^0(q)\rangle, \qquad (10)$$

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

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

where $H_C(q)$ is the Hamiltonian for the electrons in the catalyst, and $H_{int}(q)$, 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, i.e., $H_{int}(q) = 0$. 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 $\Phi_R^i(q)$ and Φ_C^k 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

$$\Phi_R^i(q) \wedge \Phi_C^k, \qquad (12)$$

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

$$\begin{aligned} E_{ik}(q) &= \langle \Phi_R^i(q) \wedge \Phi_C^k | H_R(q) \\ &\quad + H_C | \Phi_R^i(q) \wedge \Phi_C^k \rangle \\ &= E_R^i(q) + E_C^k \\ E_R^i(q) &= \langle \Phi_R^i(q)|H_R(q)|\Phi_R^i(q)\rangle \\ E_C^k &= \langle \Phi_C^k|H_C|\Phi_C^k\rangle \end{aligned} \qquad (13)$$

(we remind that the interaction between the catalyst and the reactants is zero for the moment). A
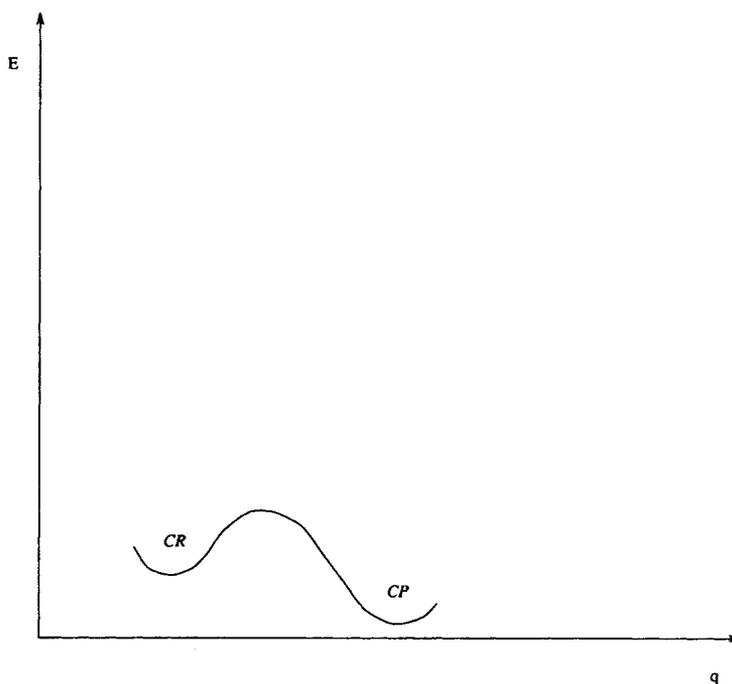
FIGURE 2. A cross-section of the PES of a transformation of the catalytic complex along the path connecting the valleys of the coordinated reactants and products. Only the nuclear coordinates of the reactants are allowed to vary; the nuclear coordinates of the catalyst are frozen.

possible picture of the cross-sections of the PES's for the several electronic states of the catalytic complex is shown in Figure 3. The shapes of all curves $E_{ik}(q) = E_R^i(q) + E_C^k$ 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 Figure 3 repeats the shape of the unreactive ground-state term of the reactants and has the same energetic barrier as that of 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 from 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 no longer 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]:

$$\Psi^0(q) = \sum_{i,k} A_{ik}^0(q)\Phi_R^i(q) \wedge \Phi_C^k, \quad (14)$$

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

Equation (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 $\Phi_R^i(q)$ and Φ_C^k are the eigenstates of the subsystem operators $H_R(q)$ and H_C, respectively, so that only the interaction operator
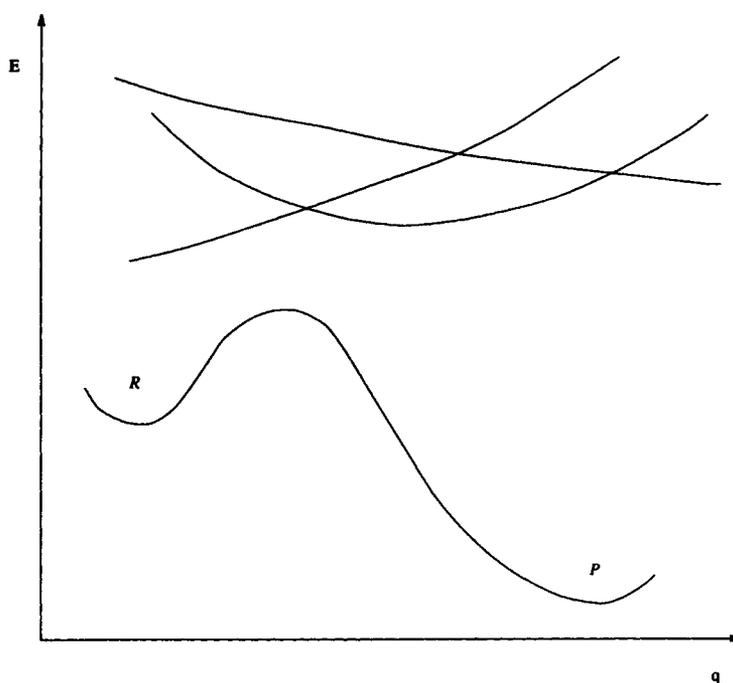
FIGURE 3. The energy profiles for the basis states of the catalytic complex (the interaction between the catalyst and the reactants is turned off).

$H_{int}(q)$ can mix the states having $i, k \neq i', k'$, we get

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

$$= \sum_{i,k} A^0_{ik}(q)^2(E^i_R(q) + E^k_C)$$

$$+ \sum_{i,k} \sum_{i',k'} A^0_{ik}(q) A^0_{i'k'}(q)\langle\Phi^i_R(q)$$

$$\wedge \Phi^k_C|H_{int}|\Phi^{i'}_R(q) \wedge \Phi^{k'}_C\rangle. \tag{15}$$

This expression serves as a basis for our further analysis. It provides an explicit form of the PES of the catalytic complex. Let 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 and 3). Let us consider a cross-section 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 path going from one

valley to another has the shape shown in Figure 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 entirely. In this case for some paths connecting the reactants with the products, the picture of the energy profiles look like that shown in Figure 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 Figure 4.
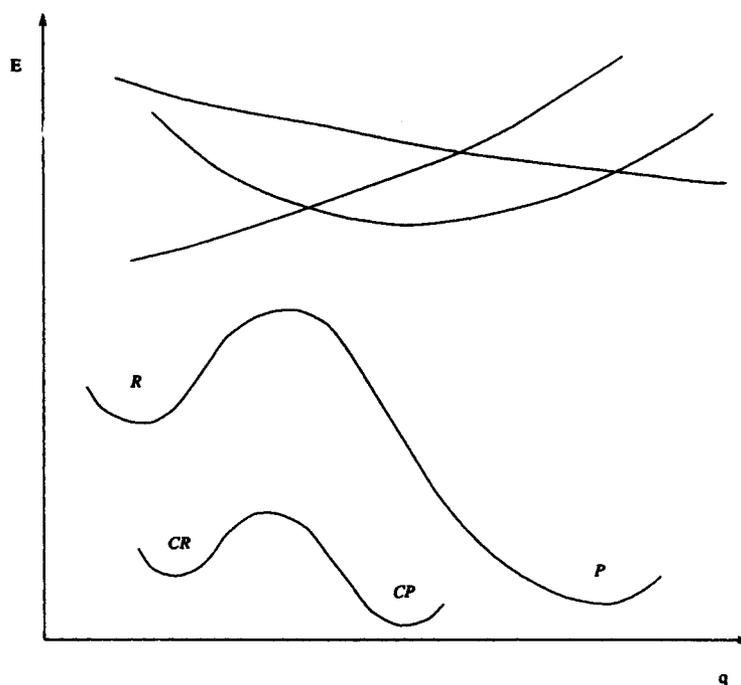
FIGURE 4. The energy profiles of the basis states of the catalytic complex and of their superposition corresponding to the ground state of the catalytic complex with the turned-on interaction.

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 Figs. 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 that is 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. Also, 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:

$$A^0_{ik}(q) \propto \frac{\langle \Phi^i_R(q) \wedge \Phi^k_C | H_{int} | \Phi^0_R(q) \wedge \Phi^0_C \rangle}{((E^i_R(q) - E^0_R(q)) + (E^k_C - E^0_C))} . \quad (16)$$

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 detail 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

$$\Delta E^i_R(q) = (E^i_R(q) - E^o_R(q))$$
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 also be small, with the hope to perform the desired process with the 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^k_C that actually controls the degree of the admixing of the reactive state and, thus, the extent of the modification of the PES. The lower this energy is, 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^k_C 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) and (16). That can be a g-factor, chemical shift, position of the absorption band in the electronic excitation spectrum, and other properties (see [3–6] for details).

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 information on the PES's of the excited states, and electron absorption spectroscopy or magnetic measurements can provide 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 present 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 obvious industrial importance of the latter (for recent reviews, 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 addresses both are basically the same. As mentioned in [10], the understanding of chemical reactivity is not possible without 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 EPS is given by the heat of chemisorption (or by the heat of formation of the catalytic complex) Q, which, in turn, depends on the reaction coordinate and must be larger for the transition 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 for this failure lies 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 a very poor performance when applied to the problem of bond formation. The reason for this, in 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 description if the canonical MO's spread over the entire system are used as a 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 access 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.

To avoid these problems, it is necessary to use a trial wave function which (i) would have the correct behavior 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 has proven to be extremely successful. It is enough to say that the famous σ–π-separation was substantiated within this approach [12]. The group function approach differs fundamentally from the MO–LCAO picture by developing the states of a composite system in terms of the states of its fragments [13, 14]. However, this approximation as it is formulated, e.g., in [11], implies that the number of electrons on each of the fragments remains fixed. That prevents satisfying condition (ii), i.e., describing the covalently, since the latter appears due tc 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 trial function covers both limits—that of the separated fragments and that of the covalently bonded ones. Apparently, this type of the function satisfies conditions (i) and (ii).

The approach presented above has been the earlier applied to the catalytic isomerization of quadricyclane to norbornadiene in the presence of the metal posphyrins 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 successfully used in [15, 16] in order to analyze qualitatively some other cases of the catalytic activity.

In this article, 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) and (ii) rather than on 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. To a 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 already been 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 a 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 it can describe 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 role 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 probably 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 the 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 the 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 of covering rather than systems, so many technical tricks are to be invented. This work is in progress now.

References

1. P. W. Atkins, *Physical Chemistry* (Oxford University Press, Oxford, 1986).

2. L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, (Pergamon Press, Oxford, 1958).

3. A. L. Tchougréeff and I. A. Misurkin, Dokl. AN SSSR **291** 1177 (1986).

4. A. L. Tchougréeff and I. A. Misurkin, Theor. Exp. Chem. **24**, 398 (1988).

5. A. L. Tchougréeff and I. A. Misurkin, Chem. Phys. **133** 77 (1989).

6. A. L. Tchougréeff, Int. J. Quant. Chem., accepted.

7. R. A. van Santen, *Theoretical Heterogeneous Catalysis*, (World Scientific, Singapore, 1991); R. A. van Santen and E. J. Baerends, in *Theoretical Models of Chemical Bonding, Part 4*, Z. B. Maksić, Ed. (Springer-Verlag, Berlin, 1991).

8. N. Koga and K. Morokuma, Chem. Rev. **91**, 823 (1991).

9. P. E. M. Siegbahn, J. Am. Chem. Soc. **115**, 5803 (1993).

10. E. Shustorovich, Adv. Catal. **37**, 101 (1990).

11. R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd ed. (Academic Press, London, 1992).

12. P. G. Lykos and R. G. Parr, J. Chem. Phys. **24**, 1166 (1956).

13. J. G. Ángyán and G. Náray-Szabó, in *Theoretical Models of Chemical Bonding, Part 4*, Z. B. Maksić, Ed. (Springer-Verlag, Berlin, 1991).

14. P. E. Schipper, Aust. J. Chem. **40**, 635 (1987).

15. A. L. Tchougréeff, Yu. V. Gulevich, I. A. Misurkin, and I. P. Beletskaya, Metallorg. Khim. **1**, 1159 (1988).

16. A. L. Tchougréeff, Yu. V. Gulevich, I. A. Misurkin, and I. P. Beletskaya, J. Organomet. Chem. **455**, 261 (1993).