Heterogeneous Catalysis

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Semiempirical Rate Constants for Complex Chemical Kinetics: First-Principles Assessment and Rational Refinement**

Matteo Maestri and Karsten Reuter**

Identifying the reaction mechanism is central to the quest towards an atomic-scale understanding of a catalytic process and represents an essential prerequisite for the nanoengineering of catalysts.[1] In essence, the reaction mechanism consists of the prevalent chemical pathways and intermediate species through which the reactants convert into the products under specific conditions. These prevalent chemical pathways are the result of the interplay among a much larger number of chemical events that can potentially occur at the catalyst surface.[2,3] Consequently, an accurate description of all these chemical events is crucial for the identification of the prevalent reaction mechanism. First-principles electronic-structure theories offer a unique possibility for accurate calculation of the kinetic parameters of elementary reactions. Nevertheless, complex processes of real technological interest may involve hundreds of reaction steps, each of which needs to be evaluated under different conditions of surface coverage and structure. The severe limitations imposed by the huge computational costs of even the most efficient present-day density-functional theory (DFT) calculations make an exhaustive first-principles computation of all the reaction steps prohibitive, except in selected model studies.[4–7]

As a result, simpler and less-demanding methods to determine activation energies are necessary for a preliminary screening of complex catalytic reaction networks.[8,9] While computationally much less demanding, the accuracy of the corresponding methods is in general uncertain. In this situation, a systematic benchmark against first-principles data for a representative range of reactions can enable an assessment of their limitations and lead to strategies to overcome them. This is what we advocate herein, by focusing as a case in point on the unity bond index quadratic exponential potential (UBI-QEP) method.[10] As a popular tool for the microkinetic modeling of complex reacting systems,[11–15] the common hybrid form of this semiempirical approach allows coverage-dependent activation energies of elementary reactions to be calculated by means of the thermochemical data of the involved species. Corresponding data, such as coverage-dependent adsorption energies, are drawn from experiments or increasingly from DFT calculations.

We start with a brief account of the UBI-QEP method.[10] The first of its two main assumptions is that in a many-body system the two-body interactions are described by a quadratic potential of an exponential function of the distance, called the bond index x. The total energy of the many-body system is then constructed from additive two-body contributions under the heuristic assumption that the total bond index of the system is conserved at unity. By using these assumptions, one arrives at simple analytical expressions for the total energy of the system as a function of the different bond indices. In a catalytic context, this would, for example, be for a diatomic molecule AB interacting with the solid surface [Eq. (1)], with the constraint $x_A + x_B + x_{AB} = 1$.

$$E_{AB}(x_A,x_B,x_{AB}) = E_{b,A}(x_A{}^2-2x_A) + E_{b,B}(x_B{}^2-2x_B) + D_{AB}(x_{AB}{}^2-2x_{AB}) \quad (1)$$

Here, $E_{b,A}$ and $E_{b,B}$ are the binding energies of the atomic species A and B at the surface and D_{AB} the dissociation energy of AB in the gas phase. Constrained minimization of this expression [Eq. (2)] leads to the minimum energy path (MEP) for the interaction and dissociation of AB at the surface (Figure 1), with $P = E_{b,A}E_{b,B}/(E_{b,A}+E_{b,B})$. The minimum of this path is related to the binding energy of AB at the surface according to Equation (3).

$$E_{AB}^{MEP}(x_{AB}) = [P + D_{AB}]x_{AB}^2 + 2[P - D_{AB}]x_{AB} + [P - E_{b,A} - E_{b,B}] \quad (2)$$

$$\min_{x_{AB}}(E_{AB}^{MEP}) = -E_{b,AB} - D_{AB} \quad (3)$$

A first estimate of the transition state (TS) of the dissociation reaction at the surface is obtained by equating it with the position on the MEP that corresponds to the fully dissociated limit ($x_{AB} = 0$) according to Equation (4).

$$E^{TS}_{AB\rightarrow A+B} = E^{MEP}_{AB}\big|_{x_{AB}=0} = [P - E_{b,A} - E_{b,B}] \quad (4)$$

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[*] Dr. M. Maestri, Prof. Dr. K. Reuter
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, 14195 Berlin (Germany)
Dr. M. Maestri
Laboratory of Catalysis and Catalytic Processes
Dipartimento di Energia, Politecnico di Milano
Piazza Leonardo da Vinci 32, 20133 Milano (Italy)
Fax: (+39) 02-2399-3318
E-mail: matteo.maestri@polimi.it
Homepage: http://www.lccp.polimi.it
Prof. Dr. K. Reuter
Department Chemie, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-2891-3616
E-mail: karsten.reuter@ch.tum.de
Homepage: http://www.th4.ch.tum.de

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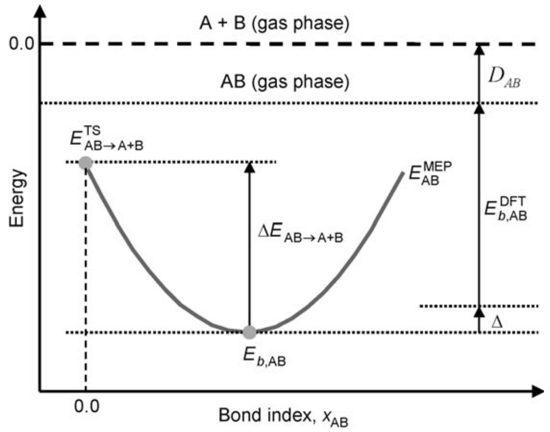

Figure 1. Illustration of the UBI-QEP minimum energy path $E^{\mathrm{MEP}}_{\mathrm{AB}}(x_{\mathrm{AB}})$ for a diatomic molecule AB interacting with a solid surface. The binding energy $E_{b,\mathrm{AB}}$ and estimate for the transition state for dissociation $E^{\mathrm{TS}}_{\mathrm{AB}\to\mathrm{A+B}}$ are shown. Note the potentially different value of the DFT binding energy $E^{\mathrm{DFT}}_{b,\mathrm{AB}}$, which then leads to a spurious contribution to the derived activation barrier for the dissociation reaction $E^{\mathrm{UBI-QEP}}_{\mathrm{AB}\to\mathrm{A+B}}$ in the prevalent parameterization procedure.

The difference between this estimate of the TS and the MEP minimum finally provides a simple algebraic expression for the activation barrier purely in terms of the thermodynamic parameters of the species involved in the reaction [Eq. (5)].

$$\Delta E^{\mathrm{UBI-QEP}}_{\mathrm{AB}\to\mathrm{A+B}} = \phi\left[(P - E_{b,\mathrm{A}} - E_{b,\mathrm{B}}) + D_{\mathrm{AB}} + E_{b,\mathrm{AB}}\right] \tag{5}$$

From this, the activation energy for the reverse process follows straightforwardly from the conservation of energy [Eq. (6)].

$$\Delta E^{\mathrm{UBI-QEP}}_{\mathrm{A+B}\to\mathrm{AB}} = \Delta E^{\mathrm{UBI-QEP}}_{\mathrm{AB}\to\mathrm{A+B}} + \left(D_{\mathrm{AB}} + E_{b,\mathrm{AB}} - E_{b,\mathrm{A}} - E_{b,\mathrm{B}}\right) \tag{6}$$

Equating the TS with the fully dissociated state will typically overestimate the true barrier. To account for the nature of the TS, $\Delta E^{\mathrm{UBI-QEP}}_{\mathrm{A+B}\to\mathrm{AB}}$ is scaled with an empirical parameter ϕ, which would be close to one for a "late" and close to zero for an "early" transition state.[16,17] Lacking any insight into the transition state, ϕ is empirically set to 0.5 in the standard formulation.

In the common hybrid approach to UBI-QEP, all the thermodynamic parameters in Equation (5) would be determined, for example, by DFT, which is still computationally much less intense than the explicit calculation of the activation energy. To test the accuracy of this approach we have performed DFT calculations for a range of dissociation reactions in the context of the water-gas shift conversion and steam reforming on a Rh(111) and Pt(111) surface. Figure 2 summarizes the obtained extended data set and compares it to the UBI-QEP-derived activation energies determined with Equation (5). To additionally check on the capability of UBI-QEP to account for coverage effects, this data set considers all reactions at the different oxygen coverage that can be realized within the employed (2×2) cells.

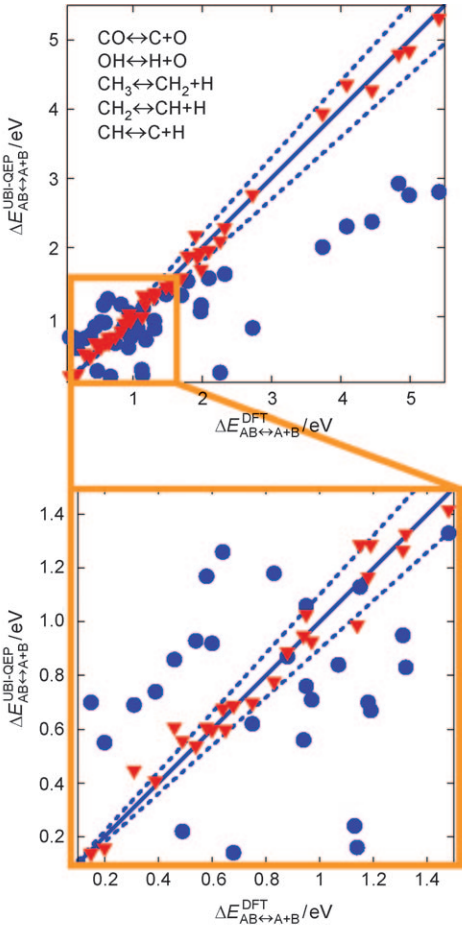

Figure 2. Benchmark of UBI-QEP derived against DFT activation energies for various dissociation reactions at Rh(111) and Pt(111) surfaces and at different oxygen coverages. Circles: standard UBI-QEP, triangles: modified UBI-QEP proposed here. The dashed lines mark a ±10% corridor around the DFT references.

In line with previous observations reported in the literature,[18] the theory–theory comparison reveals drastic deficiencies in the hybrid UBI-QEP approach commonly employed in the literature, with predicted UBI-QEP barriers deviating partly by more than 100% from the reference value. To analyze the reasons for this shortcoming we focus on the dissociation of OH at a Rh(111) surface. Figure 3 shows the computed binding energies for the adsorbed reactant OH(s) and products O(s) + H(s), as well as the explicit DFT and derived UBI-QEP barriers at the different oxygen coverages. UBI-QEP underestimates the DFT barrier at zero oxygen coverage by 0.3 eV. Considering the crudeness in the empirical choice of ϕ, a straightforward explanation for this discrepancy would be that the empirical value $\phi = 0.5$ does not grasp the true nature of the TS. The geometries of the DFT-derived transition states (Figure 3) indeed suggest that the TS is formed quite late in the reaction at all the oxygen coverages considered.[16,17] For this reaction, an adjustment of ϕ to a larger value of 0.7 brings the UBI-QEP barrier into quantitative agreement to its DFT reference at zero oxygen coverage.

Since DFT calculations revealed that the geometry of the TS does not change with coverage, the value of ϕ determined by DFT for this reaction at zero oxygen coverage should not

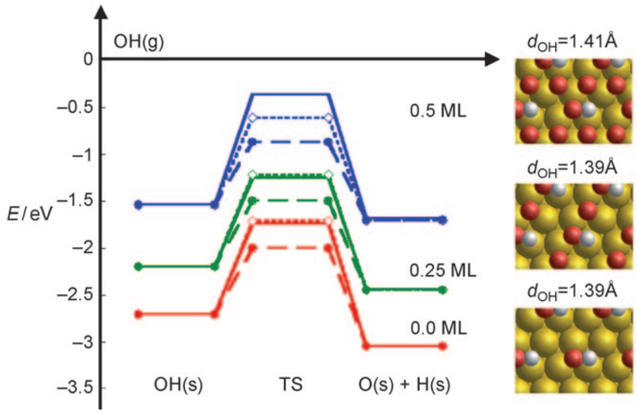

Figure 3. Computed energy profile for the OH dissociation at a Rh(111) surface at different oxygen coverages. The DFT barrier values (solid lines) versus standard UBI-QEP (dashed lines) and adjusted UBI-QEP (dotted lines) are compared. Additionally shown are top views of the different DFT-derived TS geometries (O: small red spheres, H: small white spheres, Rh: large yellow spheres).

change with coverage. Consequently, if the UBI-QEP assumptions were valid, the semiempirical method should deliver the correct coverage-dependence of the activation energy only by means of the coverage-dependent binding energies. As apparent from Figure 3, this is true at an oxygen coverage of 0.25 monolayer (ML). However, the UBI-QEP value still underestimates the true DFT barrier by 0.3 eV at an oxygen coverage of 0.5 ML. As the DFT calculations indicate no change in the nature of the TS with coverage, there is no physical justification to invoke a coverage-dependence of ϕ. Instead, this underestimation points to a shortcoming in predicting the coverage effect that is intrinsic to the hybrid UBI-QEP approach.

The reason for the shortcoming becomes apparent upon closer inspection of Figure 1. In UBI-QEP theory the binding energy of AB at the surface is a derived quantity, related to the minimum of the MEP through Equation (3). As UBI-QEP is an approximation, the corresponding value $E_{\text{b,AB}}$ must not necessarily coincide with the DFT value $E^{\text{DFT}}_{b,\text{AB}}$, even if the MEP is exclusively parameterized with DFT data, namely $E^{\text{DFT}}_{b,\text{A}}$ and $E^{\text{DFT}}_{b,\text{B}}$. Directly using $E^{\text{DFT}}_{b,\text{AB}}$ in Equation (5) as a reference for the activation barrier, as is done in prevalent hybrid UBI-QEP, therefore introduces a spurious contribution $\Delta = E^{\text{DFT}}_{b,\text{AB}} - E^{\text{UBI-QEP}}_{b,\text{AB}}$, as shown in Figure 1. There is no reason why this contribution should not vary with coverage, and thus leads to a wrong coverage-dependence in the UBI-QEP prediction. For the specific case of OH dissociation at a Rh(111) surface we find the value of Δ to vary from −0.3 eV at zero coverage to +0.3 eV at half monolayer coverage.

The root of the problem is the inconsistency between the energy of the transition state from the UBI-QEP potential and the binding energy of the diatomic molecule from DFT with respect to the zero energy reference in Figure 1. A straightforward remedy for this inconsistency in the prevalent parameterization approach is to simply shift the MEP by Δ, so that its minimum coincides with the proper DFT binding energy. On one hand, this recovers the consistency of the derived activation barriers for the forward and backward reaction with all DFT thermochemistry references, but on the other hand, it maintains the shape of the MEP as prescribed by UBI-QEP. Thus, instead of calculating the energy of the chemisorbed AB molecule through Equation (3), we directly derived this value by the analytical minimization of Equation (2). In doing so, we can rewrite Equation (5) as Equation (7) (see the Supporting Information for the derivation).

$$\Delta E^{\text{UBI-QEP}}_{\text{AB}\to\text{A+B}} = \phi\left[\Delta E^{\text{TS}}_{\text{AB}\to\text{A+B}} - \min_{x_{\text{AB}}}\left(E^{\text{MEP}}_{\text{AB}}\right)\right] = \phi\left[\frac{(P-D_{\text{AB}})^2}{(P+D_{\text{AB}})}\right] \qquad (7)$$

This expression now depends solely on atomic or gas-phase parameters, for which DFT values can be used without introducing inconsistencies from the underlying UBI-QEP relations. The DFT binding energy for the molecule AB occurs only in the parameterization for the backward reaction [Eq. (6)] to ensure the correct thermochemistry.

By using this modified parameterization procedure we achieve a significant improvement in the accuracy of UBI-QEP against the DFT reference. The coverage dependence is now fully reproduced and, as summarized in Figure 2, the obtained activation barriers fall within a 10 % corridor for the entire range of reactions included in the data set. This modification has been discussed here for the example of dissociation reactions, but can be easily generalized to other classes of reactions. Insight into the nature of the transition state needs to enter the scheme through one remaining empirical parameter. Such insight is established for many classes of reactions, but can alternatively come from selected first-principles calculations. Consequently, once the parameter ϕ has been determined, for example, by a reference DFT calculation, then the lateral interactions in the activation energies can be computed as a function of only the lateral interactions in the binding energies within a window of 10 % around the DFT data. Considering the negligible computational cost involved in determining the UBI-QEP barriers, this remaining uncertainty is perfectly acceptable. With no intention to be fully quantitative, such semiempirical estimates of the barriers can provide most useful insight into complex reaction networks, where an exhaustive first-principles treatment is prohibitive. Here, the computationally undemanding estimates of the barriers may serve as an initial approximate input for the identification of the prevalent reaction pathways that require refined kinetic parameters from explicit first-principles calculations.[19] Beyond the specific UBI-QEP framework, our study thus nicely demonstrates the necessity and virtue of a first-principles assessment of prevalent semiempirical approaches in practical catalysis research—in terms of both an assessment of the reliability and rational refinement.

Experimental Section

The calculations were carried out with the ultrasoft pseudopotential code CASTEP,[20] using the semilocal PBE functional[21] to treat electronic exchange and correlation and supercell geometries with 4 layer slabs, 12 Å vacuum separation, and a (2×2) surface unit-cell periodicity. Systematic convergence tests showed that for these cells the use of 6×6×1 Monkhorst–Pack grids[22] for the Brillouin zone integrations and a plane wave expansion up to 400 eV ensures the numerical convergence within 30 meV of the computed binding energies. The explicit DFT activation barriers were determined by first locating the TS with a climbing-image nudged elastic band, followed by a refinement and vibrational validation within the conjugate-gradient quadratic synchronous transit method.[23,24]

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