The UBI–QEP method: a practical theoretical approach to understanding chemistry on transition metal surfaces

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The UBI–QEP method: a practical theoretical approach to understanding chemistry on transition metal surfaces

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Abstract

In this review we examine the presently available theoretical techniques for determining metal surface reaction energetics. The unity bond index–quadratic exponential potential (UBI–QEP) method, which provides heats of adsorption and reaction activation barriers with a typical accuracy of 1–3 kcal/mol, emerges as the method with the widest applicability for complex and practically important reaction systems. We discuss in detail the theoretical foundations of the analytic UBI–QEP method which employs the most general two-body interaction potentials. The potential variable, named a bond index, is a general exponential function of the two-center bond distance. The bond indices of interacting bonds are assumed to be conserved at unity (up to the dissociation point), and we cite state-of-the-art ab initio calculations to support this assumption. The UBI–QEP method allows one to calculate the reaction energetics in a straightforward variational way. We summarize the analytic formulas for adsorbate binding energies in various coordination modes and for intrinsic and diffusion activation barriers. We also describe a computer program which makes UBI–QEP calculations fully automated. The normalized bond index–molecular dynamics (NBI–MD) simulation technique, which is an adaptation of the UBI–QEP reactive potential functions to molecular dynamics, is described. Detailed summaries of applications are given which include the Fischer–Tropsch synthesis, oxygen assisted X–H bond cleavage, hydrogen peroxide, methanol and ammonia syntheses, decomposition and reduction of NO, and SO₂ chemistry. © 1998 Elsevier Science B.V.

One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.

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1. Introduction

In this review we are primarily concerned with working theoretical approaches to surface chemistry and heterogeneous catalysis on transition metal surfaces. In preparing any review the first tasks are deciding which works to consider and determining how to compare and judge results. While we will discuss a variety of theoretical approaches, our main efforts will be devoted to the unity bond index–quadratic exponential potential (UBI–QEP) method. The latter provides projections of surface reaction energetics with a typical accuracy of 1–3 kcal/mol and is by far the only practical method presently available to treat a wide variety of complex systems of reactions. Accordingly, the specific purpose of this review is to provide a single, coherent source of the UBI–QEP method which contains: (a) a detailed discussion of the theoretical foundations including strengths and weaknesses of the method; (b) developments of the formulas for surface reaction energetics such as adsorbate binding energies and reaction enthalpies, and reaction and diffusion activation barriers; (c) adaptation to molecular dynamics simulations of surface chemical processes; (d) guidelines for the application of the method; and (e) a summary of the most important results.

Recent years have witnessed enormous efforts to increase the accuracy of quantum mechanical calculations of chemically interesting systems, which advanced the mainstream approaches to the level of ab initio wavefunction methods [1–10] and density functional methods [11–16]. The former are in principle more accurate and the latter more tractable although, advances such as the three-index approximation to the four-index integrals [17] are beginning to make ab initio calculations competitive with density functional calculations on a per-iteration basis. Still, accurate ab initio calculations of energetics of chemically interesting systems are prohibitively difficult or impossible. As late as 1996, it appears that “electronic structure methods have primarily been successful in treating gas-phase problems or problems in which only a very local chemical environment is important. To study ...surface chemistry... much further work is needed on soundly based methods” [18]. Remarkably, in the centennial issue of the Journal of Physical Chemistry (Volume 100, 1 August 1996), which summarized progress in all important areas of physical chemistry, among many theoretical achievements described, the quantum theory of adsorption and surface chemistry was conspicuously absent. As far as ab initio calculations are concerned, “the goal of treating chemically interesting systems containing at least 10 atoms to high accuracy using this approach seems to be far away in the future... This realization has led to a start of a new era of quantum chemistry, which has been termed the age of pragmatism” [19].

1.1. Pragmatism and chemical value

Pragmatists search for real values and practical ways to acquire them. Accordingly, we take the chemical value, which encompasses both chemical understanding and utility, as the major criterion for our selection of theoretical approaches to surface reactivity with an emphasis on the practical ones. By ‘practical’ we mean an approach, that is physically sound and useful for the practitioner in the field. Because all theoretical models are approximate, there may be no direct relation between the sophistication of a model and its usefulness. For example, in the realm of adsorption and heterogeneous catalysis, arguably one of the most useful and widely used models is that by Brunauer–Emmett–Teller (BET) [20] which is based on a number of drastic approximations and even violates the principle of microscopic reversibility [20,21]. When, to rectify these apparent flaws, a more rigorous theoretical
treatment of the BET model was made, the resulting equation produced no discernible improvement in agreement with experiment and became too cumbersome to be used [22]. The art is in finding a model adequate to the problem, and, for the pragmatist, ‘the only criterion of a molecular model is its value to chemists, assessed by its performance’ [23].

Industrial catalysts usually are complex compositions in which the catalytic metals are supported and combined with various additives (stabilizers, promoters, poisons, etc.) to achieve the proper dispersion, surface area and stability to deactivation, which is necessary for efficient long-term performance. It is unrealistic to ask the theorist to explain, let alone predict, all details of such awesome complexity. But of the possible theoretical contributions to the design of catalysts, particularly valuable for guidance would be insight into mechanisms of surface reactions. A cause for optimism is that reactions on well-defined single-crystal surfaces and (poorly defined) supported metal surfaces often have the same mechanism [24].

Arguably, the most direct theoretical approaches to surface reactivity are based on reaction energetics, particularly the reaction enthalpies and activation barriers, providing the potential energy profile of a surface reaction. Adsorbate enthalpies consist of gas-phase, molecular bond energies and adsorption energies. The gas-phase bond energies of reactants, intermediates, and products in principle are available; i.e. they can be obtained from experiment and/or accurate ab initio calculations [9,25]. The modern ab initio techniques are sufficiently advanced to predict even the energies of transition states for rather complex gas-phase reactions [26]. At the same time, experimental data on surface reaction energetics are scarce and often far from being unambiguous. So determination of the adsorption energies and activation barriers of surface reactions is often a task for theory: a difficult task.

1.2. Quantum mechanical approaches

On a microscopic level, reaction energetics should be determined by quantum mechanical methods, preferably by the most general and accurate such as first-principles ab initio and density functional (DF) methods. Remember that the DF methods depend on the adequate knowledge of the exchange–correlation potentials, and, although more and more accurate forms are constantly being developed, there is no known systematic way to achieve a prescribed level of accuracy [11–16]. At the same time, ab initio wavefunction methods allow one in principle to obtain any level of accuracy for any system, given a sufficiently powerful computer. The common feature of both ab initio and DF methods is that they are much more useful for structural predictions (calculations of bond lengths and angles, vibrational frequencies, charge moments, etc.) than for calculations of thermochemical properties [11–16]. Accurate calculations of bond energies and particularly activation barriers, which are the (small) differences between the (large) total energies of reactants, intermediates/transition states and products, are still an enormous challenge.

Although calculations of metal clusters are commonly distinguished from calculations of metal slabs, since in slab calculations a unit mesh is in effect a particular kind of cluster, eventually all quantum chemical methods make use of clusters to simulate adsorption and reaction on a metal surface. A fundamental problem is how to make metal atoms in a finite cluster represent those on a surface of the infinite bulk. The theoretical reality is paradoxical: on the one hand, one needs large enough clusters to adequately represent a geometric and electronic structure of a surface; on the other hand, only small enough clusters can be accurately treated by the available methods. A working compromise is
embedding clusters, where the immediate adsorbate environment is treated with the maximal possible accuracy but the rest with practical simplicity [27,28]. In practice, within a given computational method, the values of chemisorption energies usually are sensitive to the cluster size, metal orbital basis set, and the metal–adsorbate geometry, so big clusters with relaxed bonds usually are needed in order to obtain results that are close to experiment. So far, only a few ab initio calculations have been made at this level [29]. Typically, ab initio calculations employ various approximations in a computational scheme and are performed for one cluster size with a fixed or constrained geometry [29].

Some comments concerning the use of semi-empirical quantum mechanical methods may be helpful in this context. In semi-empirical calculations of both cluster- and slab-type, reasonable agreement with experiment can usually be reached by using ad hoc parameters. Moreover, the values of these parameters are often much different from those used for molecular calculations. The use of ad hoc parameter values blurs the conceptual picture. For example, if one employs some ad hoc energies of s, p, and d-orbitals to fit the metal Fermi energy, the absolute and even relative s, p and d contributions to the band structure and chemical bonding can hardly be illuminated. Meanwhile, on the basis of such semi-empirical calculations, particularly within the simple Hückel type framework [30], the notion of predominant d-orbital participation in transition metal–adsorbate bonding has been introduced, by analogy with coordination compounds. By contrast, the most accurate ab initio calculations of large metal clusters made so far on various 3d and 4d metals indicate that the predominant contribution to the chemisorption interaction is via metal surface s (along with p) orbitals [31–35]. In coordination compounds, the crucial role of metal d orbitals has been seen not only in various calculations but more importantly, deduced from symmetry rules which are independent of computational approximations. On metal surfaces, however, no analogous symmetry rules can be invoked, so the relative role of s, p and d-orbitals can be deduced only from computations. Here, high quality ab initio results clearly should be viewed as having the most credence. As far as conceptual understanding is concerned, no analogy borrowed from quantum chemistry of coordination compounds should be used in metal surface chemistry if it is inconsistent with results of more accurate ab initio calculations of large enough clusters.

Quantum mechanical calculations of potential energy surfaces (PESs) still encounter many conceptual difficulties [34], not to mention computational ones. In calculations of any PES, determination of minima is known to be much easier than maxima (saddle points). For an adsorption PES, the same truth holds. Here, calculations of the minima represented by heats of adsorption, already difficult, are incomparably easier than calculations of the saddle points determining the activation barriers. The saddle point represents a transition state, a theoretical construct about which direct experimental information usually is lacking. For systems of chemical interest, the geometry of a transition state may be precarious and can hardly be fixed in advance, so that the accuracy of calculations, particularly due to effects of cluster size and bond relaxation, appears to be even more important. Again, only a few ab initio methods have dealt with these challenges [29]. In most cases, drastically simpler approaches have been taken. For example, instead of calculating the activation barriers some indices of the metal surface reactivity have been defined [36].

Even if the computational results for the PES are good enough, the chemical insights and understanding are never straightforward. The more detailed the calculations, the more difficult it is to translate mathematical, quantum mechanical constructs, such as extended basis sets, configuration interactions, etc., into a chemically useful language. For example, the non-uniqueness of orbitals (either
the Hartree–Fock orbitals of molecular orbital theory or the Kohn–Sham orbitals of density functional theory) renders problematic the use of orbitals as a vehicle for interpreting chemical bonding [5,18].

1.3. Phenomenological approaches

Given such difficulties with current quantum mechanical approaches, working alternatives are desirable. The most natural option is the use of analytic phenomenological models. Perhaps, the greatest advantage of an analytic model is that through explicit interrelations among parameters it provides direct conceptual understanding. Because we are interested in surface energetics, the model parameters should be of thermodynamic origin and, ideally, be observable. Of course in order to be informative, an analytic model should have a rigorous and rigid mathematical formalism, within which the rules of the game are well defined. Most importantly, to be of general and predictive value, a model should treat the chemisorption energetics not in a piecemeal fashion but in its wholeness, i.e. both energy minima (molecular chemisorption energies) and maxima/saddle points (reaction activation barriers) should be determined in a unified way within the same formalism.

During the last decade we have been developing such an analytic phenomenological approach which describes the energetics of chemisorption and reaction on metal surfaces within a general, heuristic framework. The initial name was the ‘bond order conservation–Morse potential (BOC–MP) method’ [37–39]. The method has undergone evolutionary changes and its formalism, now fully automated, has been generalized to efficiently calculate the heats of chemisorption of diatomic and polyatomic molecules (in various coordination modes), as well as the reaction activation barriers of dissociation, recombination and disproportionation. It needs as input only atomic heats of adsorption and gas-phase molecular bond energies for projections of molecular heats of adsorption and reaction activation barriers. Experimental molecular heats of adsorption may be used directly to calculate activation barriers. Most recently, the method’s foundation was revised and found to be much more general than initially thought, and the formalism became more rigid and uniform. As explained below, these developments warrant a change of the method’s name, namely the unity bond index–quadratic exponential potential (UBI–QEP) method.

The UBI–QEP method is unique among the current theoretical approaches in that the method can be and has been successfully applied to a wide variety of complex reactions whose mechanisms might comprise tens or hundreds of intermediates and elementary steps. These are processes of real chemical interest, including many industrial heterogeneous catalytic reactions.

It should be stressed that phenomenological modeling in general and the UBI–QEP modeling in particular is not competitive with but complementary to quantum mechanical modeling. Below we explore this matter in detail and show how the two approaches have been synergistically combined. Also, all practical quantum mechanical approaches to chemisorption bonding include so many simplifying assumptions that this formally first-principles modeling is eventually heuristic, not much different from phenomenological modeling.

Model projections provide both explanations of the known and predictions of the new. Arguably, the most glamorous aspect of theoretical modeling is predictions of new things confirmed by subsequent experiment. The most valuable and lasting feature, however, is the extent to which a model is capable of coherent explanation and interrelating the whole body of relevant experimental observations. Actually, the line between model explanations and predictions is blurred. Even if the fact is known, its theoretical explanation is an internal prediction of the model. If the known facts are plentiful and seemingly
unrelated, their coherent interrelations, particularly quantitative, attest to the model’s validity no less than successful predictions of few new facts (anyway, later one usually recognizes that the right answer has been obtained by not quite right reasons).

1.4. What is in this review?

The main goal of the present review is to systematically describe the UBI-QEP method, its foundation, formalism and major applications, and give a fair analysis of the method’s strengths and weaknesses, compared to other theoretical models. Because first-principles ab initio calculations suitable for description of chemisorption and reaction of adsorbates on metal surfaces have been extensively reviewed most recently in this journal by Whitten and Yang [35], there is no need to dwell on ab initio calculations again. Instead we devote our attention to DF calculations which are becoming the staple of theoretical surface studies.

The review is organized as follows: In Section 2 we recall the theoretical approaches to chemisorption and reaction on metal surfaces. Because there are two recent reviews on this subject in this journal [35,40], our summary is brief and complementary. It appears that although the current theoretical and computation methods are in principle accurate and powerful, in practice they cannot be efficiently applied to most surface reactions of chemical interest because of the lack of practical and accurate interaction potentials.

In Section 3 we describe the foundation of the UBI-QEP method. We show that the two-body interaction potential used is the best possible one described by a polynomial under the most general physical conditions. We introduce a bond index of a two-center bond (an exponential function of the distance) and postulate its conservation at unity for all active bonds involved, in agreement with high quality ab initio calculations. The rest is a straightforward algebra of minimizing the total energy of a chemisorbed system in terms of thermodynamic observables, namely atomic adsorption energies and gas-phase molecular bond energies.

In Section 4 we present the UBI-QEP formalism for unimetallic surfaces. The analytic expressions are summarized for heats of molecular adsorption and for reaction activation barriers, both intrinsic and diffusional, and coverage effects on adsorption energetics are considered. Selected comparisons with experiment illustrate the accuracy of the model projections.

In Section 5 we describe the adaptation of the UBI-QEP formalism to molecular dynamics simulations of surface reactions.

In Section 6 we present the UBI-QEP formalism for bimetallic surfaces which is an extension of that for unimetallic surfaces.

In Section 7 we give an essence of the UBI-model computer program, which can read chemical reactions and provide for fully automated computations of the reaction energetics.

In Section 8 we illustrate how high quality ab initio calculations have been combined with the UBI-QEP ones to verify and corroborate the model projections.

In Section 9 we summarize some important UBI-QEP applications, particularly recent mechanistic studies of complex surface reactions. Examples include the periodic trends in the Fischer–Tropsch synthesis, the syntheses of methanol, hydrogen peroxide and ammonia, and SO$_2$ and NO$_x$ chemistries. Finally, results of molecular dynamics simulations of dissociation reactions of O$_2$, S$_2$, C$_2$, N$_2$, SO, and isotopically substituted derivatives, on selected fcc(1 1 1) surfaces are described from which the full Arrhenius reaction rate constants are obtained.
In Section 10 we give comparisons with other theoretical approaches, especially ab initio and density functional ones, to adsorption energetics and surface reactivity. We concentrate on the most recent examples to illustrate the current abilities of the methods.

In Section 11 we comment on the state of affairs in the UBI–QEP method, its successes, limitations and failures.

Finally, there are seven appendices which contain numerous technical (analytic and numeric) details.

2. Current theoretical approaches

Several reviews of the current theoretical approaches to adsorption and reactivity on metal surfaces have appeared in the literature recently that examine in detail specific modeling methods [35,40–43]. For example, Lombardo and Bell [40], Holloway [41], and Graham [42] have reviewed the quantum and molecular dynamics literature relevant to surface chemistry modeling. Whitten and Yang [35] have reviewed the wavefunction based ab initio surface chemistry literature. Kang and Weinberg [43] have reviewed the Monte Carlo applications to surface chemistry. In this section, we mention only some aspects of these approaches that are relevant to our purposes herein, rather than duplicate discussions already in the literature.

2.1. General overview

The bulk of the dynamics work done to date has been on diatomic dissociations of molecules composed of isotopes of hydrogen [44–50]. However, Luntz and Harris [51,52] have conducted quantum dynamics calculations of the dissociation of small alkane molecules. Jackson et al. [53] have performed dynamics studies of surface reactions involving HCl, and Kara and DePristo [54] and Haase et al. [55] have performed dynamics simulations of N2.

In classical dynamics calculations one solves Newton’s equations of motion:

\[ f_{ii} = m_i \frac{d^2 \alpha_i}{dt^2} = -\frac{\partial V(\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_n)}{\partial \alpha_i}, \quad i = 1, \ldots, n, \tag{2.1.1} \]

where \( \alpha_i \) represents either the x, y or z cartesian coordinate of atom \( i \), \( m_i \) is the mass of atom \( i \), and \( V \) is the potential energy function. This set of equations has a dimension of \( 3n \). The solution of these equations specifies the positions of the atoms as a function of time, \( \alpha_i(t) \). The total energy as a function of time is the sum of the kinetic and potential energies:

\[ E_{\text{tot}} = V(\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_n) + \frac{1}{2} \sum_i m_i v_i^2. \tag{2.1.2} \]

The temperature, \( T \), of the system is usually taken to be a time average of the kinetic energy per particle.

Quantum dynamics involves solving time-dependent Schrödinger equation for the system of interest [41]:

\[ i \frac{\partial \Psi(r; t)}{\partial t} = H \Psi(r; t). \tag{2.1.3} \]
The Hamiltonian is
\[ H = \sum_j T_j + V(r_j), \]
where \( T_j \) is the kinetic energy operator for particle \( j \) and \( V(r_j) \) is the potential energy operator. The notation is intended to convey the fact that the wavefunction and potential energy function are explicit functions of the coordinates of every particle in the system that also has kinetic energy (often some particles are represented as effective or pseudo-potentials fixed in space). The dimensionality of the wavefunction is \( 3n \), where \( n \) is the number of actual particles in the system.

The recent review of Kang and Weinberg [43] describes the present situation regarding the modeling of heterogeneous catalytic processes with Monte Carlo techniques. For thermally driven processes, the equilibrium distribution of systems over the set of possible system configurations, \( P(C_i) \), is the familiar Boltzmann distribution [43]:
\[ P(C_i) = \frac{\exp\{-H(C_i)/k_bT\}}{\sum_j \exp\{-H(C_j)/k_bT\}}, \]
where \( k_b \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( H \) is the ‘single system’ or ‘single particle’ Hamiltonian and the summation runs over all possible system configurations. The desired properties to be simulated are dependent on this probability distribution function, which is built up from a set of system configurations for which the energies are known. A probability distribution function can be constructed from a set of system configurations randomly chosen, the reliability of which depends on the size of the sample or set of randomly chosen configurations. The ‘Monte Carlo’ aspect of these applications of Boltzmann statistics is in the sampling of the configuration space. The Metropolis algorithm [56] begins with an arbitrarily chosen initial configuration and generates a configuration set according to criterion based on the relative energies of the configurations. The Kawasaki sampling algorithm [57] also constructs a configuration-to-configuration transition probability based on the energy differences between system configurations. The sampling methods allow one to avoid the usually large (huge) number of energy evaluations that one would have to consider if one computed the energy of every possible configuration of the system of interest. The energies of the members of these generated ensembles are considered to be known, which means they have to be computed.

While the usual Monte Carlo application has been to equilibrium phenomena, the simulation of time-dependent processes with Monte Carlo techniques has been addressed [43]. The simulation of rate processes requires some adaptations in the standard Monte Carlo method in order that the real time required for the physical process to occur can be estimated [43]. In order to simulate a system at equilibrium the energy differences between members of the ensemble need to be known [43]. In order to simulate time-dependent processes the energy barriers along paths that connect the different system configurations need to be known [43]. This represents an increase in the detail of knowledge one must have about the system in order to determine the length of time required for a process to occur. Kang and Weinberg [43] have stated that, in principle, quite complex systems can be treated with Monte Carlo methods. However, one must obtain physically reasonable energy differences for the configurations composing the ensemble, and in the case of time-dependent Monte Carlo simulations, one must have the transition barriers separating the configurations, otherwise the simulation time cannot be determined. In applications such as the simulation of TPD spectra, the Monte Carlo method requires
additional information in order for the pre-exponential factor to be determined, which usually is obtained from fitting to a set of experimental data [43]. Reactions involving small monomeric and dimeric adsorbates have been studied employing the Monte Carlo method [43]. Complex catalytic mechanisms have not been approached with Monte Carlo, and the burden of producing the energies and energy barriers for these systems seems to be the preventing influence.

Transition state theory (TST) offers useful expressions for the reaction rate constant, which are obtained employing assumptions of thermal and chemical equilibria [58]. The equilibria assumptions require the presence of the Boltzmann (statistical) equilibrium distribution of systems among the available energy levels. Assuming Arrhenius behavior the TST expression for the pre-exponential factor is [59]:

\[
A = \frac{k_b T \kappa_{TST}}{h \alpha q},
\]

(2.1.6)

where \( \kappa \) is a transmission coefficient, \( \alpha \) is a maximum coverage and \( q \) is the single particle partition function with the symbol, \( \uparrow \), designating the transition state.

There are several limitations with regard to applying the TST expressions to determine the Arrhenius rate constant. Firstly, the TST assumes that an equilibrium exists between the reactant(s) and the transition state, and the appearance of the Boltzmann factors comprising the commonly used single particle partition functions is indicative of the assumption of an equilibrium distribution of thermal energy among the degrees of freedom of the reacting particles and even the transition state. The pre-exponential involves the ratio of the partition functions of the transition state and the reactant. In order to evaluate this ratio, some appropriate estimate of the energy levels of the transition state and reactant must be available. This implies a detailed knowledge of the transition state which is difficult to obtain. In the important set of surface reactions that have no intrinsic activation barrier, there is no transition state in the traditional sense and TST is not applicable. The application of TST to surface reactions is further complicated by the multiplicity of possible transition states and the presence of diffusion contributions to the rate constant.

Eqs. (2.1.1)–(2.1.4) show how the potential energy surface is intimately involved with the fundamental equations of classical and quantum dynamics. The statistical approach represented by the Monte Carlo–Boltzmann statistics also presumes this knowledge of the PES as seen in Eq. (2.1.5). It is impossible to avoid having to have a detailed knowledge of the potential energy surface, and this is the largest impediment to applications of these methods to surface chemistry. In principle, these energy surfaces can be obtained from ab initio techniques, but in practice they cannot. Perhaps time rather than money is the most important limiting consideration. Using current techniques, accurate and definitive ab initio calculations of full potential energy surfaces for complex metal surface reactions simply cannot be done in a reasonable amount of time on the world’s fastest computers regardless of the monetary expense.

Whitten and Yang [35] have recently published an excellent review of ab initio calculations in surface chemistry. Although there are many examples of applications of ab initio methods to the study of static adsorbate systems, the exhaustive review of Whitten and Yang [35] reveals that today there are only four surface reactions for which there are significant ab initio treatments: the dissociations of H2 and CH4 and the recombination of H and CH4 on Ni; and the dissociation of CO on Rh.

The density functional approach to electronic structure calculations is becoming increasingly popular for modeling surface phenomena [13–16]. Traditionally, the appeal of density functional methods has been the computational ease with which the ground state electron density could be obtained for a
particular system. However, the decrease in computational effort relative to wavefunction methods usually came at the expense of accuracy. Binding energies in particular have been notoriously inaccurate in the past. As density functional methods develop, it appears that their accuracy may improve [13–16], but at the expense of computational effort and/or the inclusion of semi-empirical parameters. It is presently unclear that a successful energy functional for one system will still be successful for different systems. The proponents of density functional methods seem optimistic with regard to the promise of these methods [14–16], but as pragmatists, we make our judgment based solely on what has actually materialized to date. The contribution to surface chemistry from density functional theory (DFT) is at a similar level to that of ab initio wavefunction methods. There are examples of applications of DFT to static adsorbate systems [60], and a small number of simple reactions have been studied, most notably by van Santen and co-workers [61–66]. Similar to ab initio wavefunction methods, no application of DFT to complex surface reaction mechanisms presently exists.

The bond order conservation–Morse potential (BOC–MP) method [37–39] is a phenomenological method for modeling chemisorption energetics and reaction mechanisms on metal surfaces. This method has by far the widest range of applicability in the energetic and mechanistic modeling of chemical processes on metal surfaces. We refer to the BOC–MP (and UBI–QEP) method as ‘pheno-
menological’ rather than empirical or heuristic because it employs phenomenological, observable, thermodynamic quantities as input parameters and analytically calculates quantities relevant to phenomenological, observable, thermodynamic properties of surface adsorption and reactive systems. The method employs some experimental values but this fact does not make it wholly empirical. One of its foundation elements is a heuristic conservation constraint, but to label the whole method as heuristic denies the general qualities of other elements. The term ‘phenomenological’ captures the level at which the projections are applicable as well as the sense that the method is based heavily on information and data that are deduced from observable phenomena.

The BOC–MP method was based on three postulates: (1) In a many-body system, all forces are spherical in that they depend on distance only. (2) Each two-body A–B interaction is described by a Morse potential (MP):

\[ E(x(r)) = a(x^2(r) - 2x(r)), \]  

where the variable \( x(r) \), called an A–B bond order (BO), depends on the bond distance, \( r \), as

\[ x(r) = \exp\{-(r - r_0)/b\}. \]  

The ‘\( a \)’ parameter is the A–B bond energy at the equilibrium distance, \( r_0 \), when the equilibrium bond order, \( x_0 \), is unity by definition. The ‘\( b \)’ parameter is a distance scaling constant. (3) In a many-body system, the total bond order, \( X \), of all interacting two-center bonds is conserved at unity:

\[ X = \sum_i x_i = 1. \]  

A corollary is that the total bond energy is constructed from additive two-body contributions, Eq. (2.1.7), as

\[ E(X) = \sum_i a_i(x_i^2 - 2x_i) \]  

under the condition of bond order conservation (BOC) at unity, Eq. (2.1.9). In the above definitions, a ‘body’ means an atom or group of atoms that within this formalism may be treated as a single entity.
For atomic and diatomic chemisorption, the BOC constraint, Eq. (2.1.9), suffices to variationally calculate in a closed analytic form, exactly or in a good approximation, the stationary points of the potential energy surface (PES), without specifying the explicit form of the bond order, $x(r)$. In other words, within the BOC–MP method, the heats of chemisorption, $Q$ (energy minima), and the reaction activation barriers, $\Delta E^\ast$ (energy maxima or saddle points), are independent of the choice of $x(r)$. Accordingly, the relevant expressions for $Q$ and $\Delta E^\ast$ do not contain $x$ but only the energy parameters \{a_i\} which are thermodynamic observables (eventually they are obtained from atomic chemisorption energies, $Q_A$, and gas-phase molecular bond energies, $D_{AB}$) and the only empirical input data.

2.2. What works for the modeling of surface reaction energetics?

From the pragmatic point of view, an applicable method should produce results of acceptable accuracy within a tolerable time frame at a manageable expense. Since an error of a few kcal/mol in an activation barrier can cause a change in the calculated reaction rate of several orders of magnitude, the numeric accuracy of energetic calculations is critical. For large systems of surface reactions, ab initio wavefunction techniques do not presently meet the pragmatist’s condition of applicability above because they require prohibitively long times to produce useful results. The faster DFT methods are also presently incapable of routinely producing results of sufficient accuracy because the energy functional is not completely known and it is not known how to improve the accuracy systematically. Finally, the lack of suitable potential energy functions for all but the simplest systems renders the dynamics methods and the statistical (Monte Carlo) methods impractical to treat chemically important and complex surface reactions. In contrast, the BOC–MP method was designed to calculate energetics of various adsorbates which made the method applicable to analyze the mechanisms of surface reactions composed of tens to hundreds of elementary steps [67–75]. The accuracy of the method is addressed directly in Sections 4.9 and 9. Typically, the accuracy of the calculated values of heats of adsorption and activation barriers is within 1–3 kcal/mol.

The BOC–MP method has been applied successfully to analyze mechanisms of many reactions of practical importance such as the direct conversion of methane to methanol [67], methanol synthesis [69], hydrogen peroxide synthesis [68], the ammonia synthesis [71], NO reduction and decomposition [72], the Fischer–Tropsch synthesis [70], allyl chemistry [73] and sulfur oxide chemistry on metal surfaces [74,75]. The applicability of the BOC–MP method has been greatly expanded after the analytic formalism had been incorporated in a fully automated computer program [76], which made it practical to treat surface reactions the mechanisms of which might include hundreds of possible elementary steps.

The consistent adequacy of the BOC–MP model projections for a wide variety of metal surface reactions suggests that the theoretical and methodological ground is sound and general despite the seeming simplicity and limitations of the model postulates. Below we reexamine the postulates, generalize them, and suggest more accurate terminology which is reflected in a change of the name of the method. Specifically, we show that the quadratic equation, Eq. (2.1.7), represents the best possible description of a two-body potential by a polynomial functional of a generalized $x(r)$ satisfying very general physical requirements where $x(r)$ may be any appropriate, particularly many-term exponential function (and energy equation (2.1.7) generalizes accordingly). Because this meaning of $x(r)$ differs from that of the bond order, whatever existing definition one might take, we name $x(r)$ the bond index (BI) and postulate the bond index conservation at unity, retaining Eq. (2.1.9) but with the new and
generalized meaning of $x(r)$, which typically is some exponential function of $r$. Accordingly, we suggest a change of the name to the unity bond index–quadratic exponential potential (UBI–QEP) method. Whenever the energy minima, $Q$, and maxima (saddle points), $\Delta E^*$, do not depend on the explicit form of $x(r)$, the UBI–QEP formalism remains operationally the same as the BOC–MP formalism. Because the generalized postulates do not affect the analytic formulas and computational results of the method, the name UBI–QEP may be applied to the whole body of work in the literature that was obtained and published under the name of BOC–MP [67–75].

3. The unity bond index–quadratic exponential potential (UBI–QEP) method: foundations

In this section we generalize the postulates of the BOC–MP method expressed in Eqs. (2.1.7)–(2.1.10). We begin with geometric structures of clean and adsorbate-covered transition metal surfaces which provide the structural information for our modeling. We discuss experimental and theoretical (quantum mechanical) evidence of the quasi-spherical nature of interaction potentials and the competitive behavior of metal–metal and metal–adsorbate bonds. We introduce the notion of bond index and provide a justification of bond index conservation as the general principle of chemisorption bonding on transition metal surfaces, with the probable exception of some 5d metals, particularly Pt.

3.1. Experimental and quantum mechanical basis for bond index conservation

3.1.1. Bulk lattices and reconstruction of clean metal surfaces

Bulk lattices of simple and transition metals have either the close packed fcc or hcp structures or the slightly less densely packed bcc structure. The fcc and hcp structures have 12 equidistant neighbors, the fcc one at the vertices of a cuboctahedron and the hcp one at the vertices of a truncated trigonal prism. The bcc structure has eight nearest neighbors at the vertices of a cube and six second nearest neighbors at the vertices of an octahedron, 14% farther from the central atom [77].

The geometry of such highly symmetric structures with high coordination numbers can be best described as the packing of equal spheres. The electronic structure of these equivalent two-center metal–metal bonds can be described only if the metal valence (three) $p$ and (five) $d$ orbitals are effectively averaged to become spatially quasi-spherical, not much different from the spherical $s$ orbital [78].

Metal surface layers are formed by cutting the bulk lattice along certain directions. Although the coordination number of a surface metal atom decreases from its bulk value, it is still high, particularly for the densely packed surface layers. For example, a metal atom on the close-packed fcc(111) surface has the coordination number nine (or eight on fcc(100)). In other words, the quasi-spherical nature of the surface metal valence orbitals remains.

Traditionally, the surface layer has been modeled as a rigid, bulk-terminated layer. More recently, with advances in crystallographic methods, it has been found that the top few layers of the metal lattice are generally involved in a reconstruction which optimizes the metal bond energy [79]. Despite individual variations in the reconstruction picture, there are distinct patterns of bond relaxation and displacements of atoms. For bonds formed by a given metal atom, the general feature is that a lengthening of some metal–metal distances is accompanied by a shortening of others, the latter being most pronounced with a decrease of the metal coordination number, which is the extreme of M–M bond lengthening.
For clean metal surfaces, this competitive bond behavior manifests in oscillatory changes in the interlayer spacing: a contraction of the outermost layer spacing with oscillations decaying rapidly into the bulk. These changes are more pronounced for more open surfaces, say fcc(110), and, are discernible even for close packed surfaces such as fcc(111). However, there are a few reports of apparently anomalous cases when the first to second layer distance expands relative to the bulk interlayer spacing. This anomalous relaxation was reported for Pt(111) [80], Pd(111) [81], Pd(100) [82], and Rh(100) [83]. The Pd and Rh studies are of insufficient quality, but in the Pt(111) case, the expansion appears to be real [81] and is of significance to us, as discussed below. Examples are given in Figs. 1(a) and (b) for surfaces of the non-transition metal, Al(110), and transition metals, Rh(111) and Pt(111), respectively.

There are more complex reconstruction patterns than the interlayer distance shifts discussed above which include lateral displacements of atoms, changes in the surface layer density, buckling of the layers, and, most dramatic of all, the fcc(110) missing row reconstruction [79]. Remarkably, large-scale reconstructions are most pronounced or even limited to the 5d metals. For example, the reconstruction of a square fcc(100) surface to a near hexagonal arrangement, the so-called hex phase, which corresponds to an increase in the surface atomic density of about 20%, was observed only for the late 5d metals, Ir, Pt and Au [79,84]. An fcc(110) surface is the most open of the widely studied low Miller index fcc surfaces, and since it has the highest surface energy of the set of low index surfaces, it is most likely to reconstruct [79]. Indeed, the clean fcc(110) surface of Ir, Pt and Au spontaneously
reconstructs, giving rise to the (1 × 2) missing row structure [79,85]. At the same time, the fcc(110) surfaces of the studied 3d metals, Ni and Cu, and 4d metals, Ag and Pd, appear to be stable to this reconstruction [79].

This distinguished behavior of the 5d metals, particularly Pt, is indicative of substantial differences in the nature of bonding in the 3d and 4d versus 5d metal surfaces. Quantum mechanical explanations of the reconstruction usually are given in terms of surface stress which, in turn, relates to the redistribution of the s, p and d electron density [79]. We return to this point below.

3.1.2. Reconstruction of atomic adsorbate-covered metal surfaces

The geometry of surfaces, covered by atomic adsorbates, provides the structural information for the UBI–QEP modeling, where the atomic binding energy depends on the coordination number of the adsorbate (cf. Eq. (4.2.1)). This number is determined by a metal–adatom arrangement in the actual reconstructed surface. Because such arrangements appear to be more discernible on regular and densely packed surfaces, we concentrate on the most symmetric ones, with mirror plane and rotational symmetries, namely, fcc(111) and hcp(0001), having three-fold symmetry, and fcc(100) and bcc(100), having four-fold symmetry.

Atomic adsorbates produce the simplest and most regular form of overlayer on metal surfaces. In general, adatoms occupy the hollow sites with maximum coordination numbers. The adsorbate-induced reconstruction usually tends to restore the contraction of the top interlayer spacing to the bulk values and causes lateral displacements of the metal atoms. On more open surfaces, where an adatom can penetrate the hollow site to bond to second layer metal atoms, one typically observes the vertical metal displacement which buckles the appropriate metal layer and increases the effective coordination number of the adsorbate [79,87]. These geometric patterns can be understood in terms of spherical adsorbate packing, where the metal–adsorbate bonds manifest the competitive behavior similar to that of the metal–metal bonds described above.

Consider the adsorbate geometries in more detail. On the close-packed fcc(111) surface, the preferred atomic adsorption site is the three-fold hollow site of which there are two types: fcc hollow sites having a second layer metal atom beneath the hollow, and the hcp hollow sites which have no second layer metal atom beneath the hollow. The three-fold sites are so tightly packed and the metal interlayer spacing is so large that the adatoms usually do not penetrate deeply enough to form a direct bond with a metal atom in the second metal layer [79,87]. Nevertheless, the drive to occupy higher coordination sites may be strong enough to cause proper reconstruction of fcc(111) surfaces. For example, S and C on Ni(111) induce a pseudo-fcc(100)–(2 × 2) overlayer structure on top of an fcc(111) substrate with the effective coordination number of four [79,87].

The hcp(0001) surface is structurally similar to the fcc(111) one: only the third and deeper metal layers differ between the two cases. The deeper hcp layers have ABABAB... registries rather than the ABCABC... registries of fcc metals [87]. Therefore, on hcp(0001) surfaces there are coordination sites with the same symmetries and the same hcp and fcc three-fold sites as on fcc(111) surfaces. There exists the same difficulty for an adatom to penetrate and bond to the second metal layer. Although the penetration into octahedral near-surface interstitial sites has been reported in a few cases limited to early transition metals, for example N/Ti(0001) [88] and C, N and O/Zr(0001) [89], the structures were not resolved in detail [89]. Thus, at least for the middle and late transition metals, atomic adsorbates, occupying the three-fold hollow sites on fcc(111) and hcp(0001) surfaces, typically have the coordination number three, and on rare occasion, four.
On most fcc(100) surfaces, adatoms occupy four-fold hollow sites, usually inducing some form of relaxation and buckling [79, 87]. For example, oxygen atoms produce the Ni(100)-p(2 × 2)-O structure, where the O atom occupies a four-fold site with the second layer Ni atom directly below the adsorption site displaced downward away from the adsorbate, suggesting the repulsive, anti-bonding interaction [90]. The effective coordination number of O is four.

Oxygen atoms on Cu(100) induce a rather complex reconstruction leading to the Cu(100)-(2√2 × √2)R45°-O structure, with every third row in the (010) direction missing [91]. Because of the missing rows, the O atoms occupy positions of relatively low coordination, pseudo-three-fold [91]. Moreover, strongly bound adatoms such as C and N on Ni(100) [92] and N on Cu(100) [93] induce the dramatic ‘clock reconstruction’, when the mirror plane symmetries are broken at the adsorption sites, while the glide plane symmetry occurs [87]. This reconstruction produces pseudo-five-fold coordinated sites on the surfaces [79]. Specifically, for the Ni(100)-(2 × 2)-C system, the surrounding Ni atoms were found to move away from the adsorption site and rotate about it, opening up the site without significantly altering the Ni–Ni spacing in the top layer, which increased by only 4%. The C atom is nearly coplanar with the first layer Ni atoms, and the in-plane C–Ni distance of 1.82 Å is close to that of 1.99 Å for the second layer Ni atom [94], which suggests an attractive, bonding interaction. In summary, for an adatom in the hollow fcc(100) site, the effective coordination number may be between three and five, but, typically is four.

The bcc(100) surface has a lower atomic density compared to the fcc(100) surface, and therefore is more susceptible to adopt high coordinations in bonding to adsorbates [79]. For example, N atoms on the bcc W(100) surface form a simple c(2 × 2) overlayer structure with the pseudo-five-fold coordination in the hollow adsorption site [95]. Moreover, the N atom was found to be closer to the second layer W atom than to the surface layer atoms, having distances of 2.13 and 2.27 Å, respectively [95]. In general, an adatom in the hollow bcc(100) site has the effective coordination number of five.

One should stress, however, that the above large-scale reconstructions changing the effective coordination number, n, were found for relatively large coverages corresponding to periodic structures amenable to a crystallographic analysis. It is quite possible that, at low coverages, the surface reconstruction and resulting change in n may be less severe, but these local and non-periodic structures may be unseen in crystallographic studies (indirect spectroscopic characterization might be made but it is not definitive).

We draw some conclusions from the above summary of surface reconstruction. First, if adsorption occurs even on highly symmetric surfaces, the real atomic arrangements may vary significantly depending on the nature of the surface and adsorbate. Because the actual coordination geometry and bond distances may be far from the bulk (and a priori assumptions about them may be wrong), theoretical modeling should not be very sensitive to the geometric details. Secondly, because the atomic binding energy, Q, depends on the adsorption geometry, it would be highly desirable to use as a model parameter the experimental value of Q which eventually takes into account the surface reconstruction.

### 3.1.3. Dominant role of LUMOs

Experimentally it is well known that on chemisorption, the formation of metal adsorbate M–AB bonds via a contact atom A (see Fig. 2(a)) results in a weakening of the internal A–B bond. This fact forms the basis of bond activation by catalytic metals.

There have been numerous attempts to explore and quantify this qualitative pattern. The simplest explanation is based on a quantum mechanical picture of HOMO/LUMO interactions. Graphical
images of molecular orbitals responsible for the bonding interaction between metal surfaces and adsorbates have been published for various systems [30,31,38,96,97]. In the frontier orbital picture (Fig. 2(b)) it is the HOMO/LUMO interactions between the adsorbate and the surface that are responsible for the bonding interaction that results when an adsorbate approaches a surface. The interaction between the HOMO of the adsorbate and the HOMO of the surface is essentially repulsive because they are both fully occupied (Pauli repulsion). The HOMOs of the adsorbate interact with the LUMOs of the surface tending to move electron density from the adsorbate to the surface because this interaction mixes an occupied adsorbate orbital with an empty surface orbital. This interaction is responsible for the ‘donor’ character of the adsorbate. LUMOs of the adsorbate interact with HOMOs of the surface tending to move electron density from the surface to the adsorbate because this interaction mixes an occupied surface orbital with an empty adsorbate orbital. This interaction is responsible for the ‘acceptor’ character of the adsorbate. Since most adsorbates are acceptors, the contribution of the LUMO orbitals is dominant [30,31,38,96,97], and the LUMOs are usually of anti-bonding character with respect to the A–B bond.

As an example, in the Hartree–Fock molecular orbitals of chemisorbing SCH$_3$ in the sulfur down mode, one sees the LUMO orbitals of the adsorbate dominating the bonding interaction with the surface [31]. These adsorbate LUMO orbitals have anti-bonding character with regard to the bonds between the contact atom and other adsorbate atoms [31]. As the bonding interaction develops between the contact atom and the surface, the bonds between the contact atom and other atoms in the adsorbate weaken. This is the quantum mechanical origin of the competitive behavior of the bond indices, and the importance of the anti-bonding LUMO orbital interactions have been analyzed in detail in the literature [30,31,38,96,97]. Even the electron correlation part of the surface–adsorbate bonding interaction can be attributed to these types of orbital interactions. By considering the occupation numbers of the CI natural orbitals [98], which diagonalize the one-particle density matrix, one sees that the adsorbate LUMO
orbitals, having anti-bonding character within the adsorbate, become more occupied as the surface bond develops [99].

For M\textsubscript{n}–AB adsorption, the described competition of the surface-A versus A–B bonds reflects valence limitations of the contact adatom A. A similar competition exists for bonds formed involving the metal atoms of the surface. From various quantum mechanical models [100] it follows that the A–M and M–B bond competition is the cause of the apparent repulsive character of the indirect interaction of coadsorbed atoms A and B sharing the same metal surface atom M. This competition appears to govern overlayer patterns when, for a given stoichiometric coverage, the preferred structure typically corresponds to the minimal (or not at all) metal atom sharing by coadsorbates [100]. This is a more justified explanation than the common one relating the overlayer structures to direct adsorbate–adsorbate repulsive interactions [100]. For example, for sulfur overlayers on various fcc(100) and bcc(100) surfaces, in particular on Pt(100), the S–S distances in the c(2 × 2) structure are larger than those in sulfides and van der Waals structures, so the repulsion between sulfur atoms is unlikely to be caused by lateral interactions [100,101].

3.1.4. Valence limitations and conservation of bond characteristics

Qualitatively, competition between bonds formed by a given atom is indicative of its valence limitations. The ultimate limitation would be conservation of some bond characteristics while the bonds are making and breaking along the minimum-energy path. In order to quantify this picture, various quantum mechanical indices have been correlated with bond energies. Commonly the indices are based on overlap matrix elements. Particularly popular is the quantum mechanical bond order introduced by Mulliken [102] and widely used ever since with endless variations. In particular, Mayer [103,104] defined ab initio two-center bond orders in terms of sums of products of density matrix elements and overlap matrix elements. All those indices are intrinsically ambiguous, however, because they are not observable and heavily dependent on the computational method used. A good example is a work by Lendvay [105] who has analyzed the utility of various bond orders obtained from ab initio calculations. For several diatomic molecules, Lendvay compared the dependence on bond length of the Mayer bond order, obtained from small basis set ab initio calculations, as well as other bond orders and their relations to various valence indices and structure-reactivity correlations. The relations were found to be informative, although not quantitative and often with qualitative inconsistencies, particularly for the geometries far from equilibrium [105].

Given the intrinsic difficulties with the non-observable quantum mechanical bond orders, quantitative correlations of the bond energy with phenomenological, observable parameters, rather than with such quantum mechanical indices described above, would be conceptually more convincing and practically more useful. One of the most convenient observables is the bond distance or some function of the distance, e.g., the exponential bond order of Eq. (2.1.8). For this phenomenological bond order, its conservation at unity has been verified in high quality ab initio calculations of linear three-center reactions in the gas phase [106–109], where the bond interactions are spherical (dependent on bond distances only), by definition. The generalization of Eq. (2.1.8) as a many-term exponential function (see Eqs. (3.4.1) and (3.4.3)) is called a generalized bond index, and its conservation at unity for many-body quasi-spherical interactions has been tested by Sellers [110–112]. Specifically, Sellers performed high quality ab initio calculations (relativistic effective core potential (RECP) Hartree–Fock + electron correlation) of the reaction energy profiles for chemisorption and dissociation of diatomic molecules H\textsubscript{2}, O\textsubscript{2} and F\textsubscript{2} on very large clusters simulating fcc(111) mercury surfaces. Then the generalized
bond indices (which Sellers called dynamic Morse potentials) were used within the UBI–QEP formalism. Sellers found [111] that through the entire range of internuclear distances in the dissociation reactions, the UBI–QEP energies typically reproduced the ab initio ones within an RMS error of 0.004 hartree.

3.1.5. Deviations from conservation rules

Quantum mechanical analysis also reveals that, in principle, there may exist non-competitive conditions of the M + A–B interaction when formation of the M–A bond may eventually strengthen the A–B bond. In particular, this situation may sometimes occur when the AB molecule is σ-bonded utilizing a lone pair occupying a HOMO. For diatomic A–B and polyatomic A–Bₙ molecules formed by atoms with s and p electrons, the HOMO is a linear combination of s and p orbitals with the nodal structure resulting in s anti-bonding and p bonding contributions to the A–B bond strength [113]. For this reason, the effect of the donor–acceptor σ-M→A–B bond on the A–B bond strength may be bonding, non-bonding or anti-bonding depending on the relative values of the opposing s and p contributions, which are determined by the nature of M, A, and B. Typically, the effect is antibonding [113], similar to that of the back-bonding π-M→A→B discussed in Section 3.1.1, and leading to the bond competition. However, for some molecules, such as PF₃, the effect is bonding resulting in strengthening of the P–F bonds on the M–PF₃ coordination [113], which is a clear deviation of the conservation rules of competitive interactions.

Another example of the non-competitive interactions may be the CO coordination where the donor–acceptor σ-M→CO bond may strengthen the C–O bond. Indeed, the C–O vibrational frequency, ωᵣ, increases from CO to CO⁺, being 2170 and 2214 cm⁻¹, respectively [114]. Thus, if the donor–acceptor σ-M→C–O bond is predominant, the CO adsorption cannot be treated within the UBI–QEP method. If, however, the back-bonding π-M→C–O prevails, the UBI–QEP method should be quite appropriate. Unfortunately, despite an enormous amount of theoretical studies of CO adsorption, the nature of the M–CO bonding on many metal surfaces, particularly on heavy 4d and 5d metals, is far from clear. We return to this matter in Section 10.4.

3.2. Quasi-spherical adsorbate–surface interactions

We have already touched the subject of quasi-spherical interactions in Sections 3.1.1 and 3.1.2. Now, we discuss it in more detail. The metal–metal interactions in bulk transition metals appear to be quasi-spherical in the sense that they distinctly depend on the M–M distance but show no discernible angular dependence. The main supportive arguments are the following:

1. Both transition s'dⁿ⁻ʸ(y = 0, 1, 2) and simple s'(y = 1, 2) metals have the same densely packed (by spheres) crystal lattices, namely fcc, hcp and bcc [115]. The fcc and hcp structures have 12 equidistant neighbors (at the vertices of a cuboctahedron and truncated trigonal prism, respectively) and the bcc structure has eight nearest neighbors (at the vertices of a cube) and six second nearest neighbors (at the vertices of an octahedron 14% further away from the central atom) [77].

2. For bonding in transition and simple metal solids, there exists an apparently universal relationship between energy and distance [116].

3. In transition metal solids, the d-shell anisotropy is averaged out, the occupancies of five d sub-bands are very close, and for many purposes the d-band may be effectively represented by a
degenerate s-type band \cite{78}. In particular, regularities of the metal cohesion energy can be well described within the constant d-density approximation \cite{77}.

On highly symmetric, low index, and densely packed surfaces, the metal atoms still have the large numbers of nearest neighbors, e.g., nine for fcc(111) or eight for fcc(100). These numbers are high enough to keep the M–M interactions quasi-spherical, as follows from the similar orbital compositions of the bulk and surface band structures found in various calculations \cite{78(c)}.

The quasi-s (spherical) nature of the metal surface orbitals makes the M–A interactions (interactions between a surface metal and an adsorbate atom A) quasi-spherical as well. The theoretical support comes from high quality ab initio calculations on large clusters of 3d and 4d metals \cite{117,118} which indicate that surface bonding arises largely from the metal s band with minor contributions from the p and d bands. The experimental support comes from the fact that on highly symmetric surfaces, adsorbate atoms, regardless of their nature, occupy hollow sites with the highest metal coordination number, for example, three-fold sites on fcc(111) or four-fold sites on fcc(100) surfaces.

For less symmetric, high-index and more open surfaces, where the metal coordination number is reduced and neighboring atoms may not be equidistant, the metal p and d orbitals may form more directional bonds in which case the interactions between the metal and adsorbate atoms may become far from quasi-spherical.

3.3. The two-body interaction potential

If the pairwise interactions between the adsorbate atoms and the atoms of the metal surface are functions of the internuclear distances, \( r \), only, the potential between two interacting bodies may be mathematically described as a polynomial functional of the variable, \( x = x(r) \), which is defined in Eqs. (3.4.1) and (3.4.3):

\[
E = \sum_i a_i x(r)^i. \tag{3.3.1}
\]

This ensures that the interaction energy is single-valued and everywhere differentiable.

We are not aware of any case in which the molecular desorption potential energy function, in the perpendicular direction from a well-defined surface binding site, has more than one minimum with respect to the distance from the surface. Certainly, potentials describing adsorption followed by bond dissociation or a change in binding site may possess more than one minimum; however, we restrict our discussion here to just the adsorption/desorption potential. We consider that a physically realistic representation of the non-dissociative chemisorption potential energy should have one and only one extremum, and that this requirement results in no loss of generality. (There presently exist no high quality ab initio calculations that indicate that there is a barrier in the potential energy of non-dissociative adsorption of molecules into a well-defined binding site on a clean surface.) In addition, since the reference point or zero in potential energy is a matter of choice it causes no loss of generality to put the energy reference point for the two-body potential at infinite separation. These two requirements of the two-body potential energy bring the functional form to the quadratic one with no constant term:

\[
E = a_2 x^2(r) + a_1 x(r). \tag{3.3.2}
\]
At equilibrium the first and second derivatives of the energy are
\[ \frac{dE}{dx} = 2a_2x_0 + a_1 = 0, \]
\[ \frac{d^2E}{dx^2} = 2a_2 > 0, \]
where the equilibrium value of \( x(r) = x(r_0) = x_0. \)

Eq. (3.3.3) describes the interrelation between the coefficients \( a_1 \) and \( a_2 \) and the numerical constant \( x_0 ): 
\[ a_1 = -2a_2x_0, \quad \text{or} \quad x_0 = -a_1/2a_2. \] 

and the two-body interaction energy becomes
\[ E = a_2[x^2(r) - 2x_0x(r)], \]
with the minimum value of energy being
\[ E_{\text{min}} = -a_2x_0^2. \]

An infinite number of two-body potentials belong to the class of potentials described by Eq. (3.3.2), and depending on the definition of \( x(r) \), may contain as many adjustable parameters as desired. Some common two- and three-parameter potentials belonging to this class are the Fues potential, \( x(r) = \text{constant}/r \) [119]; the Lennard-Jones ‘6-12’ potential, \( x(r) = (r_{eq}/r)^6 \) [120]; and the Morse potential, \( x(r) = \exp\left\{-\left(R - R_{eq}\right)/a\right\} \) [121]. Other potentials involving polynomials of higher degree can be constructed that have a single non-zero extremum, for example
\[ E = x^3[a_2x(r)^2 + a_1x(r)]. \]

In Appendix A we show that, for \( n > 0 \), such forms allow multiple extrema in the desorption potential of diatomic molecules and are rejected on that basis.

So far, the function, \( x(r) \), is unspecified and the numerical value of \( x(r_0) = x_0 \) is indeterminate. As shown below, due to the flexibility of the \( x(r) \) function, the two-body interaction potential, Eqs. (3.3.2) and (3.3.6), accurately represent any two-body interaction energy that possesses a single energy minimum regardless of the value of \( x_0 \). This claim of completeness is justified in Section 3.4. In principle we are at liberty to select any value we wish because any choice of \( x_0 \) simply brings about a rescaling of the ratio of the coefficients \( a_2 \) and \( a_1 \). There are, however, compelling reasons for one particular choice of \( x_0 \), namely, \( x_0 = 1 \), as discussed below. With this choice of \( x_0 \), the two-body interaction energy is
\[ E = a_2[x^2(r) - 2x(r)] \]
and the minimum value of the energy is
\[ E_{\text{min}} = -a_2. \]
so that the two-body binding energy is
\[ Q = -E_{\text{min}} = a_2. \]

3.4. The bond index

The general features of the variable, \( x(r) \), are as follows: (a) there should be a one-to-one correspondence between \( x(r) \) and \( r \); (b) \( x(r) \) is non-negative \( (x(r) \geq 0) \); (c) \( x(r) \) monotonically decreases to zero as \( r \) increases without bound; and (d) at equilibrium \( x(r_0) = 1 \).
As the atomic and diatomic wavefunctions are known to have exponential radial parts, it is natural to try exponential functions to represent \( x(r) \). In particular exponential functions of the form

\[
x_j(r_j) = \sum_i c_i \exp\left\{-\frac{r_j - r_{0,j}}{b_j}\right\}, \quad j = 1, n.
\] (3.4.1)

possess the above general features. In the illustration of an adatom, A, in an fcc(1 1 1) three-fold hollow binding site, \( n = 3 \) (Fig. 3), we will refer to these exponential functions, \( x_j(r_j) \), as the two-body bond index. The infinite sets, \( \{c_i\} \) and \( \{b_i\} \), are adjustable fitting parameters that could be determined by fitting the energy expression, Eq. (3.3.9), to the exact interaction energy. The conditions (b) \( x_j(r_{0,j}) \geq 0 \), and, (d) \( x_j(r_{0,j}) = 1 \) require

\[
\sum_i c_i = 1, \quad c_i \geq 0.
\] (3.4.2)

The exponential form of every term in the summation guarantees that the long range asymptotic limit will be correct. The bond index, \( x_j(r_j) \), can be generalized further as

\[
x_j(r_j) = \sum_{i,k} c_{ik} \exp\left\{-\frac{(r_j - r_{\text{ref},k})}{b_i}\right\},
\] (3.4.3)

where the expansion coefficients must satisfy

\[
\sum_{i,k} c_{ik} \exp\left\{-\frac{(r_{0,j} - r_{\text{ref},k})}{b_i}\right\} = 1.
\] (3.4.4)

Here, \( r_{0,j} \) is the equilibrium value of the inter-body distance and \( r_{\text{ref},k} \) is \( k \)th reference distance, which is not necessarily the equilibrium distance. The functions defined in Eq. (3.4.3) employ \( \{c_{ik}\} \), \( \{r_{\text{ref},k}\} \) and \( \{b_i\} \) as adjustable parameters and are analogous to off-center s functions in quantum chemistry. These functions are capable of describing oblate shapes as well as spherical shapes. Requiring the \( \{c_i\} \) and \( \{c_{ik}\} \) to be fixed, non-negative constants independent of the molecular environment disallows negative values of \( x_j(r_j) \) in all situations. Also, the \( x_j(r_j) \) function should not have any wiggles of sufficient magnitude as to give rise to more than one value of \( x_j(r_j) \) for any given \( r_j \) as this would violate the required one-to-one correspondence between \( x_j(r_j) \) and \( r_j \).
In principle the summations in Eqs. (3.4.1) and (3.4.4) are infinite, and the set of all such terms forms a complete set of functions for the expansion of any arbitrary function that obeys the same boundary conditions. The completeness is demonstrated by analogy to completeness arguments in quantum chemistry: the set of all spherical Gaussian functions is a complete set for the expansion of any spherical function that obeys the same boundary conditions. Similarly, any \( x_j(r_j) \) obeying the proper boundary conditions can be accurately represented as an (infinite) expansion of functions defined by Eqs. (3.4.1) or (3.4.4). Therefore, the exact \( x_j(r_j) \) and the two-body interaction potentials are in principle accurately described in the UBI-QEP method.

When the summation in Eq. (3.3.1) contains a single term, the two-body interaction potential, Eq. (3.3.9), becomes a Morse potential. When the bond index, Eq. (3.4.1) or its generalization as Eq. (3.4.3), contains a single term, it formally resembles the Pauling bond order for a single bond formed by a shared electron pair [122]. For all other situations, the bond index described by Eq. (3.4.1) has no relation to the Pauling bond order.

3.5. Unity bond index conservation: principle of chemisorptive bonding

In Section 3.3 we discussed the mathematically indeterminate nature of the equilibrium value of the bond index, \( x_0 = x(r_0) \), and said that there are compelling reasons for choosing the value of \( x_0 = 1 \). Consider now these reasons. At the equilibrium distance, \( r_0 \), any bond index, \( x(r) \), defined by an exponential function (Eq. (3.4.1)) will be equal to unity regardless of the nature, particularly the multiplicity, of the bond (e.g. H-H, C≡O). If one goes from a two-body system to a many-body system, where the total bond index, \( N \), of the bonds involved is conserved, it should be conserved to \( N = x_0 \). This is understood by considering a system in which there are several active bonds.

Consider a straightforward example of the CO molecule adsorbed in an ontop site, M, as shown below.

\[
\begin{array}{c}
O \\
\parallel \\
C \\
\mid \\
M
\end{array}
\]

The sum of the M–C and C≡O bond indices, \( x_{\text{M–C}} \) and \( x_{\text{C≡O}} \), respectively, is equal to the constant \( N \). When the C≡O bond is dissociated giving gas-phase atomic oxygen and leaving the carbon atom in the ontop site, \( x_{\text{C≡O}} = 0 \) and the \( x_{\text{M–C}} \) bond index is equal to its equilibrium value, \( x_{0,\text{M–C}} \), which is equal to the normalization constant, \( N \). When the CO molecule is desorbed from the surface, \( x_{\text{M–C}} \) is zero and \( x_{\text{C≡O}} \) is equal to its equilibrium value, \( x_{0,\text{C≡O}} \), which is equal to the normalization constant, \( N \). Since the two bond index equilibrium values are equal to the same constant, \( N \), they are equal to each other. In other words, the equilibrium values of the two bond indices are the same regardless of the fact that the multiplicities of the bonds are different.

In general, the total bond index for this system is \( \sum_j x_j(r_j) = N \), where \( N \) is the normalization constant. When all but one bond is dissociated so that all but one bond index vanishes, the sum has only one term: \( x_j(r_0) = x_{0j} = N \). Therefore, the value of the equilibrium bond index, \( x_{0j} \), is the value to which the total bond index is conserved. Repeating this argument for every value of \( j \) in \( x_j(r_0) = N \)
requires that all the equilibrium values of the two-center bond indices, \( x_{oi} \), must be the same and equal to \( N(x(r_{oi}) = x_{oi} = N \) for all \( i \)). Therefore, the precise form of the normalization condition for the total bond index, \( X \), along a minimum energy path is

\[
X = \sum_i x_i(r_i) = N = 1. \tag{3.5.1}
\]

The choice of \( x_{oi} = N = 1 \), for all \( i \), is needed in order for the \( a_2 \) parameter to be the strength of the two-body interaction potential in Eq. (3.3.6). Bond index conservation to unity, \( N = 1 \), has been verified by ab initio calculations employing exponential bond index functions for linear, three-center bonds [105–109]. More importantly, bond index conservation to unity has been verified by ab initio calculations on adsorption and dissociation of diatomic molecules \( \text{H}_2, \text{O}_2, \) and \( \text{F}_2 \) on close-packed metal (Hg) surface [111]. Therefore, we postulate the following principle of chemisorptive bonding: the sum of the two-body bond indices of the active bonds along any minimum energy path of a metal surface reaction is conserved and equal to unity.

Certainly further high-quality ab initio calculations on chemisorptive systems are needed to test the scope and accuracy of the unity bond index (UBI) principle. Meanwhile, we will use this heuristic principle to obtain various quantitative predictions that may be directly compared with experimental results. The consistency of the agreement will manifest the value of the heuristic UBI principle.

The UBI condition together with the requirement of minimum energy (with respect to the independent bond indices) determine changes in all the bond indices along a minimum energy path when an additional interacting body is included. Therefore, a many-body potential capable of describing the minimum-energy path can be constructed from additive two-body potentials under the UBI condition which effectively accounts for various many-body contributions. For example, for a diatomic \( \text{AB} \) adsorption shown in Fig. 4 the UBI constraint is

\[
x_{\text{AB}} + x_A + x_B = 1. \tag{3.5.2}
\]

In other words, the total energy of a many-body system can be expressed as a summation of additive two-body bond energies governed by the UBI condition. The normalization of the total bond index to

\[
\frac{x_{\text{AB}}}{x_A + x_B + x_{\text{AB}}}
\]

Fig. 4. Admolecule AB in a bridge metal surface binding site (metal atoms are shown by open circles). The two-body bond indices are denoted as \( x_A, x_B \), and \( x_{\text{AB}} \).
unity is an important and distinctive feature of the bond index conservation within the UBI–QEP method. Also, for practical reasons the sum over the pairwise interaction energies is limited to nearest neighbors within a metal surface unit mesh or binding site.

The postulates on which the UBI–QEP method is based can be summarized as:

1. The two-body interaction potential is spherical in that it depends only on the interbody distance.
2. The two-body interaction energy possesses a single minimum and goes to zero monotonically as the distance increases without bound.
3. The two-body potential is expressed as a polynomial functional of an exponential variable called the bond index.
4. The multi-body potential energy is formed by summing the nearest neighbor pairwise interactions constrained by the unity bond index conservation.

These postulates, being much more general and justifiable than those of the BOC–MP method (see Section 2.1), form a more firm and logical theoretical basis. In operational terms, however, the UBI–QEP and BOC–MP methods practically do not differ, in particular the UBI–QEP equations to calculate the molecular heats of adsorption and intrinsic activation barriers remain the same as the BOC–MP equations. Nevertheless, the logical arguments and algebraic transformations that lead to these equations are more general and uniform and we present them below.

4. UBI–QEP analytic formalism for unimetallic surfaces

4.1. Atomic heats of adsorption

We begin with the simplest case of atomic chemisorption on unimetallic surfaces. An energy function, $E$, describing atomic chemisorption is the sum of the $n$ pairwise interactions between the adatom, A, and the $n$ metal atoms of the surface, M, that form the $M_n$ binding site or unit mesh

$$E = Q_0 \sum_{i} [x_i^2(r_i) - 2x_i(r_i)],$$

(4.1.1)

where the summation runs from 1 to $n$. The $Q_0$ parameter, which describes the strength of the two-center M–A interaction and is independent of the crystal plane, replaces the $a_2$ parameter of Section 3.3. As stated in the above rules, the summation will be limited to the nearest neighbor metal atoms, or equivalently, the number of metal atoms defining the binding site, e.g. $n = 1$ for ontop, $n = 2$ for bridging and $n = 3$ for fcc(111) hollow, $n = 4$ for fcc(100) hollow, $n = 5$ for bcc(100) hollow as shown in Fig. 5. As explained in Section 3.1.2, because the fcc(111) and (100) surfaces are densely packed, without large-scale reconstruction the metal atoms from the second layer are not nearest neighbors and therefore are considered to be not coordinated with A. Unlike $n = 4$ for fcc(100), the coordination of $n = 5$ for bcc(100) can be realized because bcc(100) is not densely packed and the fifth metal atom from the second layer may also be a nearest neighbor (being at the same or even shorter distance as the four metal atoms of the top layer) and available for coordination with A.

To obtain the atomic binding energy, Eq. (4.1.1) is optimized under the unity bond index constraint of Eq. (3.5.1). The details of this optimization are described in Appendix A and the correspondence
between bond index space optimization and coordinate space optimization is discussed in Appendix B. The resultant $n$ M–A interactions are equivalent and the atomic binding energy is [38,39]:

$$Q_{nA} = -E(n) = Q_{0A}(2 - 1/n).$$

As a result of the unity bond index conservation, this expression has a dependence that is less than linear on the adsorbate coordination number, $n$, which is in agreement with experimental information [38,39].

Some general statements based on the UBI–QEP method can be made regarding atomic adsorption on metal surfaces. Firstly, the method predicts that for an adatom, $A$, chemisorbing in an $n$-fold site, $M_n$–$A$, the A–M interactions are equivalent and therefore the local structure will have $n$-fold symmetry. Secondly, Eq. (4.1.2) predicts that the most stable binding site for an atom will be the one with the highest coordination of surface atoms, namely the hollow site. This is in excellent agreement with experimental evidence for all atoms [38,39,79,87]. (The occasional exception is hydrogen which sometimes occupies bridge sites [38]. However, the bridge coordination of hydrogen is also a particular
consequence of unity bond index conservation because the small size of hydrogen can make each two-center M–H bond index less than 1/n, so a hollow site becomes less favorable [38]. A specific model projection is that, without reconstruction effects, atoms will be more strongly bound in the hollow site of the fcc(100) surface (n = 4) than in the hollow site of the fcc(111) surface (n = 3), the energy difference being $Q_{0A}(1/3 - 1/4) = Q_{0A}/12$.

We stress that we evaluated the energy expression for the adsorption of atoms, Eq. (4.1.1), without knowing the geometry parameters. It was not necessary to determine the adatom–surface, adatom–metal or metal–metal equilibrium distances and corresponding valence angles (see Appendix A). This ‘geometry blind’ aspect of the UBI–QEP method is one of its major features and represents a tremendous computational advantage. In practice the $Q_{0A}$ parameters are obtained from experimental heats of adsorption, $Q_A(n)$, whenever possible by working in reverse with the help of Eq. (4.1.2):

$$Q_{0A} = Q_A(n)/(2 - 1/n).$$  \hfill (4.1.3)

Here, n might be 3, 4 or 5 depending on whether the experimental atomic heat of adsorption, $Q_A(n)$, corresponds to a three-fold fcc(111) or hcp(001) hollow, four-fold fcc(100) hollow or a five-fold bcc(100) hollow adsorption.

For ideal surfaces with n equivalent M–A bonds, Eq. (4.1.3) is exact within the UBI–QEP framework. Real surfaces may reconstruct and change the effective coordination number, n. In Section 3.1.2 we saw that mono- and di-valent atomic adsorbates such as H and O usually do not change n, but, tri- and tetra-valent adatoms, such as N and C, often do. For example, C atoms reconstruct the Ni(111) surface and eventually occupy four-coordinated sites [86]. The C atoms also reconstruct the Ni(100) surface and become effectively five-coordinated [92]. The increase in n from 3 to 4 to 5 increases the coefficient, $2 - 1/n$ in Eq. (4.1.3), from 1.67 to 1.75 to 1.80, respectively. In other words, not knowing the actual coordination number may create uncertainties in $Q_{0A}$ of the order of 5%. The actual uncertainty may be even smaller if the experiment shows no distinct anisotropy in the value of $Q_A$ for different surfaces having different values of n. In particular, for the discussed Ni(111) and (100) surfaces, experimental atomic binding energies, $Q_{c}$, were reported to have practically the same value of 170 kcal/mol for ill-defined coverages [123].

An account of the adsorbate coverage may further mitigate the uncertainties in $Q_{0A}$. We have already mentioned that large-scale reconstructions increasing n were observed for large coverages. From Eq. (4.1.3), for a given experimental value of $Q_A$, an increase in n leads to a decrease in $Q_{0A}$. Because the value of $Q_A$ generally decreases with coverage (see Section 4.8), for a fixed, unreconstructed n, the smaller high-coverage value of $Q_A$ also corresponds to a decrease in $Q_{0A}$.

In summary, the use of experimental data for $Q_A$ provides for the energetic effects of adsorbate-induced surface relaxation, including the metal–metal bonds involved, that are automatically taken into account. The accurate (enough) scaling of $Q_{0A}$ from $Q_A$ can be made by using Eq. (4.1.3) with the ideal value of n on densely packed, symmetric crystal planes, without exact knowledge of the coordination geometry. In other words, the values of $Q_{0A}$, being rather close on different surfaces, are a characteristic of the metal but not a particular surface. Table 1 compiles averaged $Q_{0A}$ values for atoms of common interest on surfaces of major fcc transition metals. Although some uncertainties in the values of $Q_{0A}$ are inevitable and may be of the order of 5 kcal/mol, their effect on calculated heats of molecular adsorption, as shown below, is further reduced by an order of magnitude.
Table 1
Suggested UBI-QEP values of $Q_{O\Delta}$ (kcal/mol) for selected adatoms and metals

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>33.6</td>
<td>31.2</td>
<td>27.6</td>
<td>37.8</td>
<td>37.2</td>
<td>36.6</td>
</tr>
<tr>
<td>O</td>
<td>61.8</td>
<td>48.0</td>
<td>45.0</td>
<td>69.0</td>
<td>52.3</td>
<td>51.0</td>
</tr>
<tr>
<td>N</td>
<td>69.0</td>
<td>60.0</td>
<td>58.2</td>
<td>81.0</td>
<td>78.0</td>
<td>69.6</td>
</tr>
<tr>
<td>C</td>
<td>72.0</td>
<td>87.0</td>
<td>84.0</td>
<td>102.6</td>
<td>96.0</td>
<td>90.0</td>
</tr>
<tr>
<td>S</td>
<td>52.6</td>
<td>46.8</td>
<td>48.0</td>
<td>67.2</td>
<td>57.0</td>
<td>55.2</td>
</tr>
</tbody>
</table>

Values are obtained from experimental atomic binding energies [38,39,253] on the appropriate fcc(1 1 1) surfaces via Eq. (4.1.3) with $n = 3$ for H and O on all metals and C on Ni. Other $Q_{O\Delta}$ values are estimated or deduced from molecular heats of adsorption by solving the UBI-QEP molecular binding energy equations for $Q_{O\Delta}$. References for experimental atomic binding energies of H, O, N, C, and S, respectively, are listed below by metal. Parentheses indicate more than one reference for that adatom. Adatoms for which the corresponding $Q_{O\Delta}$ value above is an estimation are indicated by ‘est’: Cu – ([255,256], [257], est, est, [258], Ag – [259], ([255,260], est, est, [258], Au – (est, [260]), [260], est, est, (est, [126]), Ni – ([255,256], ([261,262], [255], [123], [258], Pd – [255], [255], [255], [256], est, Pt – [263], [255], [255], [256], [258].

Table 2
Gas-phase bond energies $D_{AB}$ (kcal/mol) for selected diatomic AB molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>A-B bond</th>
<th>$D_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>H-H</td>
<td>103</td>
</tr>
<tr>
<td>O$_2$</td>
<td>O-O</td>
<td>119</td>
</tr>
<tr>
<td>N$_2$</td>
<td>N-N</td>
<td>226</td>
</tr>
<tr>
<td>CO</td>
<td>C-O</td>
<td>256</td>
</tr>
<tr>
<td>NO</td>
<td>N-O</td>
<td>151</td>
</tr>
<tr>
<td>SO</td>
<td>S-O</td>
<td>125</td>
</tr>
<tr>
<td>OH</td>
<td>O-H</td>
<td>102</td>
</tr>
<tr>
<td>CH</td>
<td>C-H</td>
<td>81</td>
</tr>
<tr>
<td>NH</td>
<td>N-H</td>
<td>75</td>
</tr>
<tr>
<td>SH</td>
<td>S-H</td>
<td>82</td>
</tr>
</tbody>
</table>

All data from Ref. [125].

4.2. Heats of adsorption of diatomic molecules

We consider below the chemisorption of a diatomic, AB. Our convention is to indicate individual, two-center A–M, B–M and A–B bond indices with italicized $x$ while non-italicized $x$ indicates a group bond index. If the quantity can be either, then non-italicized $x$ is used. Throughout this work, the quantity, $D_{AB}$, is the enthalpy of the reaction that breaks the AB bond, i.e., the gas-phase AB bond energy. The values of $D_{AB}$ for some diatomic AB molecules are given in Table 2.

4.2.1. Weak binding

This type of binding is typical for closed-shell molecules such as CO, N$_2$ or molecular radicals with strongly delocalized unpaired electrons, such as O$_2$ or NO. Because the heats of adsorption are relatively low (~10–35 kcal/mol) we refer to this as weak binding.
Consider first the coordination of the AB molecule with atom A as the contact atom and atom B directed away from the surface, which allows us to neglect the M–B interactions. For the n-fold coordination, the UBI–QEP energy is the sum of the pairwise potentials

\[ E(n) = Q_{0A} \sum_i (x_{A,i}^2 - 2x_{A,i}) + D_{AB}(x_{AB}^2 - 2x_{AB}). \]  

(4.2.1.1)

The UBI constraint is

\[ \sum_i x_{A,i} + x_{AB} = 1. \]  

(4.2.1.2)

The summation runs over the n interactions between adatom A and the metal atoms of the binding site. The minimization of Eq. (4.2.1.1) under the UBI constraint is described in Appendix A. The binding energy for such a mono-coordination via atom A is [38,39]:

\[ Q_{AB,n} = \frac{Q_{0A}^2}{Q_{0A}/n + D_{AB}}. \]  

(4.2.1.3)

Although Eq. (4.2.1.3) gives a slightly larger binding energy for binding sites of higher coordination (n = 2, 3, etc.) than for ontop coordination (n = 1, Eq. (4.2.1.4)), this result may be an artifact of neglecting the repulsive M–B interactions which also increase in magnitude with n [38,39]. These binding energies are too close for the UBI–QEP method to make reliable predictions regarding the preferred binding site. However, precisely because the energies are so close, the energetic differences have no significant effect on the reaction activation barriers predicted by the UBI–QEP method (see below). Another consequence of neglecting the M–B repulsive interaction is that Eqs. (4.2.1.3) and (4.2.1.4) may be particularly inaccurate for mono-coordination of homonuclear diatomics [38,39].

Experimentally for mono-coordinated, closed-shell molecules, the ontop binding (n = 1) site is typically preferred, and the UBI–QEP heat of adsorption is

\[ Q_{AB} = \frac{Q_{0A}^2}{Q_{0A}/n + D_{AB}}. \]  

(4.2.1.4)

An immediate model prediction is that the atom having the higher heat of adsorption will be the favored contact atom.

Because a contact adatom is bound in an ontop site, di-coordination of a diatomic, AB, via both A and B, should typically span a bridge site.

Then the UBI–QEP energy is

\[ E_{AB} = Q_A(x_A^2 - 2x_A) + Q_B(x_B^2 - 2x_B) + D_{AB}(x_{AB}^2 - 2x_{AB}). \]  

(4.2.1.5)

and the UBI constraint is

\[ x_A + x_B + x_{AB} = 1. \]  

(4.2.1.6)
The energy minimization, taking into account the effective non-zero adsorbate coverage, is discussed in detail in Ref. [38], and in this paper in Section 4.8 and Appendix F. The resulting formula for the binding energy is [38,39]:

\[
Q_{AB} = \frac{ab(a + b) + D_{AB}(a - b)^2}{ab + D_{AB}(a + b)},
\]

(4.2.1.7)

where

\[
a = \frac{Q_{0A}^2(Q_{0A} + 2Q_{0B})}{Q_{0A} + Q_{0B}} \quad \text{and} \quad b = \frac{Q_{0B}^2(Q_{0B} + 2Q_{0A})}{Q_{0A} + Q_{0B}}.
\]

(4.2.1.8)

(4.2.1.9)

Eq. (4.2.1.7) has a simple form for homonuclear diatomics, A_2:

\[
Q_{A_2} = \frac{3Q_{0A}^2}{6Q_{0A} + 16D_{A_2}}.
\]

(4.2.1.10)

This equation is of particular importance because, as mentioned above, there is no good formalism to describe the mono-coordination of erect A_2.

The above formulas for Q apply to any AB molecule, either acceptor or donor. With respect to a metal surface, the acceptor adsorbates are much more common than the donor ones [38,39]. For donor adsorbates, the UBI–QEP method projects two other A–B coordination modes. First, one can place AB parallel to a surface and above a metal atom, M, in the ontop site:

\[A----B \quad | \quad M\]

This case of the donor AB → M bonding is described by Eqs. (4.2.1.7)–(4.2.1.10) [124]. Secondly, AB may be positioned parallel to a surface and across the M–M bridge:

\[A \quad M------M \quad B\]

For this case of the donor AB → M_2 bonding, the heat of adsorption is [124]:

\[
Q_{AB} = 2\left[\frac{ab(a + b) + 2D_{AB}(a - b)^2}{ab + 2D_{AB}(a + b)}\right],
\]

(4.2.1.11)

where

\[
a = \frac{3Q_{0A}}{4} \quad \text{and} \quad b = \frac{3Q_{0B}}{4}.
\]

(4.2.1.12)

(4.2.1.13)
For a homonuclear donor A₂, one obtains

\[ Q_{A₂} = \frac{9Q₀²_{A₂}}{(3Q₀²_{A₂} + 16D_{A₂})}. \]  

(4.2.1.14)

Comparison of Eqs. (4.2.1.14) and (4.2.1.10) reveals that Eq. (4.2.1.14) yields a higher binding energy than Eq. (4.2.1.10). We stress that Eq. (4.2.1.14) should not be applied to acceptor adsorbates.

4.2.2. Strong binding

Molecular radicals such as OH, SH, CH, etc., that have substantially localized, unpaired electrons, behave similar to atoms with respect to their binding site preferences and prefer the same high coordination site as would the bare contact atom. Because of this, the potential, \( E_c \), that describes the interaction between the contact atom and the metal surface, may be described as

\[ E_c = Q_A(x_A^2 - 2x_A), \]  

(4.2.2.1)

where \( x_A \) is the group bond index between the contact atom A and the surface. For the erect chemisorption of the molecular radical, the UBI–QEP energy expression is

\[ E = Q_A(x_A^2 - 2x_A) + D_{AB}(x_{AB}^2 - 2x_{AB}) \]  

(4.2.2.2)

and the UBI conservation is

\[ x_A + x_{AB} = 1. \]  

(4.2.2.3)

Minimization of this energy under the constraint of unity bond index (see Appendix A) gives the binding energy [38,39]:

\[ Q_{AB} = \frac{Q_A^2}{(Q_A + D_{AB})}. \]  

(4.2.2.4)

Here again, an immediate model prediction is that the atom with the higher heat of adsorption will be the favored contact atom. Because these radicals tend to be strongly bound (~35–120 kcal/mol) we refer to this as strong binding.

4.2.3. Medium binding

Heats of molecular chemisorption span a wide range, 10–120 kcal/mol. The previous sections describe the extremes of weak and strong binding. It is useful to consider also intermediate binding and it may be described by interpolating between these two extremes. The simplest interpolation is the arithmetic average of the two extremes [38,39]:

\[ Q_{AB} = 0.5\left[\frac{Q_{0A}}{Q_{0A} + n + D_{AB}} + \frac{Q_A^2}{Q_A + D_{AB}}\right]. \]  

(4.2.3.1)

The methyl radical, \( \text{CH}_3 \), is an example of an adsorbate for which we employ the medium binding formula.

A set of rules for determining which formula to use in a specific situation is given in Section 4.5. Diverse examples of calculations employing the above formulas are collected in Table 8.

4.3. Heats of adsorption of polyatomic adsorbates

The treatment of polyatomic adsorbates is a straightforward extension of the diatomic treatment. Now the symbols A and B represent groups of atoms and the parameter, \( D_{AB} \), is usually the enthalpy
Table 3
Gas-phase bond energies $D_{AB}$ (kcal/mol) for selected polyatomic AB molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>A–B bond</th>
<th>$D_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>O–C–O</td>
<td>127</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>O–N–O</td>
<td>73</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>O–S–O</td>
<td>132</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>O–S–O</td>
<td>83</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>C–H</td>
<td>182</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>C–H</td>
<td>293</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C–H</td>
<td>398</td>
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<tr>
<td>H$_2$O</td>
<td>H–O</td>
<td>119</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>H–O–O</td>
<td>88</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>N–H</td>
<td>169</td>
</tr>
<tr>
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<tr>
<td>C$_2$H$_6$</td>
<td>H–C–CH$_3$</td>
<td>106</td>
</tr>
<tr>
<td>HCOOH</td>
<td>HCOO–H</td>
<td>106</td>
</tr>
</tbody>
</table>

*All data from Ref. [125].

of the reaction that separates the A atom group from the B atom group in the gas phase. In some cases, particularly for weakly bound admolecules such as ‘π-bonded’ ethylene, the A and B atom groups are treated as pseudo-atoms for which we derive $Q_{0A}$ and $Q_{0B}$ parameters. In the pseudo-atom treatment the $Q_{0A}$ parameter is the heat of adsorption of the A (or B) atom group in the ontop site. In other cases, usually for more strongly bound admolecules, the $Q$ or $Q_0$ parameters for the contact atoms are used. The values of $D_{AB}$ for some polyatomic AB molecules are given in Table 3.

4.3.1. Mono-coordination

Mono-coordination of polyatomic adsorbates is the most direct analog when the adsorption energy can be described by Eqs. (4.2.1.3) and (4.2.1.4) or Eq. (4.2.2.4). The case of HSCH$_3$ illustrates the treatment of weakly bound, closed-shell polyatomics. Assuming sulfur is the atom that contacts the surface, A is the sulfur atom and B represents H and CH$_3$. The definition of $D_{AB}$ is the enthalpy of the gas-phase reaction that breaks the AB bond(s):

$$A–B(g) \rightarrow A(g) + B(g),$$

$$H–S–CH$_3$(g) \rightarrow S(g) + H(g) + CH$_3$(g). \quad \Delta H = D_{AB}.$$  \hspace{1cm} (4.3.1.1)

Since closed-shell molecules usually bind in ontop sites, the heat of adsorption of HSCH$_3$ is given by Eq. (4.2.1.4), where $Q_{0A} = Q_{0S}$ and $D_{AB}$ is defined in Eq. (4.3.1.1). On Au(111), where $Q_{0S} = 48$ kcal/mol (Table 1) and $D_{AB} = 154$ kcal/mol [125], the ontop binding energy of HSCH$_3$ obtained
from the UBI–QEP Eq. (4.2.1.4) is 11.4 kcal/mol which agrees well with the experimental value of 12.1 kcal/mol [126]. Other examples are given in Table 2.

4.3.2. Di-coordination

The di-coordination of polyatomic adsorbates as quasi-diatomic AB is described by the general Eqs. (4.2.1.7)–(4.2.1.10), but, now the parameters for A and B relating to M–A and M–B interactions are rescaled to reflect the specifics of polyatomic A–B bonding.

4.3.2.1. Symmetric di-coordination

Molecules such as acetylene, HC≡CH; ethylene, H₂C=CH₂, and hydrogen peroxide, HO–OH are treated as quasi-homonuclear diatomics, A₂. Here the contact atoms are designated as atoms A, and $D_{A2}$ is the enthalpy needed to break the bonds between atom A and the rest of the molecule, which is also the total gas-phase energy of the bonds formed by the A atom. The heat of adsorption of acetylene, e.g., is computed with Eq. (4.2.1.10) with the atom A representing carbon and $D_{A2}$ representing the enthalpy of the gas-phase reaction

$$\text{HCCH} \rightarrow \text{C} + \text{H} + \text{CH}. \quad (4.3.2.1.1)$$

For acetylene on Pt(1 1 1) the parameters $D_{A2}$ and $Q_{OA}$ are 311 and 90 kcal/mol, respectively [38,39,125], and the heat of adsorption in the bridge site from Eq. (4.2.1.10) is 13 kcal/mol which lies in the middle of the reported experimental range 9–18 kcal/mol [127].

4.3.2.2. Asymmetric di-coordination

When A and B represent dissimilar atom groups, then the heat of adsorption is given by Eqs. (4.2.1.7)–(4.2.1.9) with the $Q_{OA}$ and $Q_{OB}$ parameters interpreted as the heat of adsorption of A and B, respectively, in the ontop site, and, the $D_{AB}$ parameter is the enthalpy required to break the A–B bond(s) in the gas phase. In this treatment the A and B atom groups are treated as pseudo-atoms. An example is the asymmetric di-coordination of OCH₂. Atom A is the oxygen and B is the CH₂ group, which is treated as a pseudo-atom. The $D_{AB}$ parameter is the gas-phase bond energy of the O–C bond, 178 kcal/mol [125]. The $Q_{O}A$ parameter is $Q_{OA}$ (51 kcal/mol for O on Pt(1 1 1): Table 1) and $Q_{OB}$ is the heat of adsorption of (the pseudo-atom) group, CH₂, in the ontop site given by

$$Q_{OB} = Q_{O}^c/Q_{O}c + D_i, \quad (4.3.2.2.1)$$

where $Q_{O}c$ is the $Q_0$ value for the contact atom in the B fragment and $D_i$ is the enthalpy required to break the bonds between the contact atom and the rest of the atoms in fragment B. In the OCH₂ example, carbon is the contact atom of fragment B ($Q_{OC} = Q_{OC} = 90$ kcal/mol for Pt(1 1 1)), and $D_i = 183$ kcal/mol is the enthalpy required to break the two C–H bonds in CH₂. Eq. (4.3.2.2.1) gives $Q_{OB} = Q_{OCH₂} = 29.7$ kcal/mol and the heat of adsorption of H₂CO in the asymmetric di-coordinated mode is predicted to be 14.5 kcal/mol from Eqs. (4.2.1.7)–(4.2.1.9). Experimental values of $Q_{H₂CO}$ on Pt(1 1 1) do not seem to be available, but a value of 15 kcal/mol has been reported for Ru(000 1) [128].

The pseudo-atom treatment is described in Refs. [37(g),39]. Since a pseudo-atom is, in reality, a group of atoms, the internal bonds within the pseudo-atom respond to various binding situations. We refer to this response as the pseudo-atom internal relaxation. The internal relaxation in the pseudo-atom that occurs when the atom group (pseudo-atom) binds in the ontop site is taken into account in the $Q_0$ parameter for the pseudo-atom. However, when an adsorbed pseudo-atom binds with another adsorbate,
there is no further accounting for additional internal relaxation within the pseudo-atom. For example, the adsorption of acetylene could be modeled as the adsorption of a pseudo-homonuclear diatomic, A–A, where A is a pseudo-atom representing the CH atom group. The $Q_{0A}$ parameter is the CH pseudo-atom binding energy in the ontop position. The $Q_{0A}$ parameter accounts for the C–H bond relaxation upon binding in the ontop site. However, when the A–A bond (C≡C) forms, no additional C–H bond relaxation is taken into account. Neglecting the C–H relaxation that occurs when the C≡C bond forms may cause a significant error. The pseudo-atom treatment is useful for cases in which the bond between the pseudo-atom and the other adsorbate is a traditional single bond.

4.3.2.3. Chelating coordination

The binding of chelates, A–X–B, where X is far from the surface so that there is no significant X-surface bonding, is treated as a special case of quasi-diatomic binding.

In chelates, there is no direct A–B bonding, so we put $D_{AB} = 0$ in Eqs. (4.2.1.7)–(4.2.1.9). As in the case of asymmetric di-coordination, the $Q_{0A} = Q_{0AX}$ and $Q_{0B} = Q_{0BX}$ parameters are the ontop site heats of adsorption for AX and BX, respectively, so the heat of chelated adsorption is [39]:

$$Q_{AXB} = Q_{0AX} + Q_{0BX} - \frac{Q_{0AX}Q_{0BX}}{Q_{0AX} + Q_{0BX}}.$$ (4.3.2.3.1)

An example of adsorption of HCOOH is given in Table 8. It is worth mentioning that CO$_2$ cannot be suitably treated as a chelating adsorbate because it is a linear molecule and the carbon is too close to the surface to neglect its interactions with the metal atoms [38,39].

4.4. Neglected repulsive interactions

As mentioned before, Eqs. (4.2.1.3) and (4.2.2.4) are derived neglecting the interactions of atom B with the surface. The justification for neglecting these interactions is that the B atom is relatively far from the surface and therefore the interactions between B and the surface should be small. Since the mono-coordinated (via A) AB molecule is typically erect on the surface, there must be some repulsive interactions between the surface and atom B which cause the adsorbate to stand erect [38]. These repulsive terms would tend to decrease the heat of adsorption. Shustorovich [38] has considered these neglected interactions in detail, and has shown that they are responsible not only for the erect geometry, but also for the preference that closed shell molecules have for surface sites of lower coordination. Although Eq. (4.2.1.3) predicts a slightly larger binding energy for molecules going to binding sites of higher coordination, this may be an artifact. For these reasons, the UBI–QEP formulas may not be appropriate to distinguish between binding sites that are close in energy. This,
however, practically does not affect the values of the calculated activation barriers for surface reactions (see Section 4.6).

4.5. Guidelines for which formulas to use

One does not always know a priori or from experiment what coordination mode or surface binding site a given molecular adsorbate will prefer. (For example, there is still no consensus in the surface science community regarding the preferred binding site of NO on Ni surfaces [129].) In such cases, the first step is to select a binding site and coordination mode for the adsorbate, and often this may involve testing a number of possibilities. The UBI–QEP method predicts that the atom with the highest atomic heat of adsorption will be (one of) the contact atom(s) provided it is not sterically hindered. In the development of the various formulas for the binding energies different approximations are made, and the UBI–QEP method cannot distinguish between binding sites if the energy differences between them are within a few kcal/mol. However, if the energy differences between the candidate chemisorption modes and binding sites are not small, say equal to or greater than 10 kcal/mol, one can reasonably use the UBI–QEP method to predict a preferred coordination mode [75].

Once the coordination mode and binding site are chosen, the second step is to decide on a formula to use for the heat of adsorption of the adsorbate. This is not as difficult as it may seem at first. For molecular radicals having a localized radical electron(s), such as OH, SCH3, CH3O and so on, one uses the strong binding formula, Eq. (4.2.2.4). Molecular radicals having localized electrons behave more like atoms and are better able to form stronger bonding interactions with the surface than they would if the radical electrons were delocalized over the adsorbate. Molecular radicals such as O2 and NO have delocalized radical electrons and one employs the weak binding formula in Section 4.2.1 for calculations of the heats of adsorption in these cases. Intermediate binding occurs in mono-valent molecular radicals that contain a tetra-valent central (contact) atom such as CH3. In these cases one averages the binding energies obtained from Eqs. (4.2.1.2) and (4.2.2.4). Closed shell molecules such as H2O, NH3, CH3OH, etc. are treated as weakly binding systems and Eq. (4.2.1.2) is used to determine the heat of adsorption. Ontop sites are usually preferred by closed shell molecules.

These guidelines can be summarized as follows:

1. Select various plausible binding sites and coordination modes based on experimental data or intuition, and try them to see what effect on the final results the various possibilities have.
2. Use the strong binding formula, Eq. (4.2.2.4), for molecular radicals having localized unpaired electrons.
3. Use the weak binding formulas, Eqs. (4.2.1.3)–(4.2.1.14), for closed shell molecules and molecular radicals having delocalized unpaired electrons.
4. Use the medium binding formula, Eq. (4.2.3.1), for mono-valent radicals having tetra-valent contact atoms.

4.6. Intrinsic activation barriers for surface reactions

In the UBI–QEP approach the intrinsic reaction barrier associated with a surface dissociation reaction is developed from a variational procedure and an interpolation. The variational procedure gives the UBI–QEP mathematical expression for the Lennard-Jones energy maximum which is an
overestimation. The interpolation is a correction for this overestimation. A detailed discussion has been given by Shustorovich [39]. Here and in Appendix D we develop the activation barrier in an equivalent way.

4.6.1. Dissociation and recombination

To facilitate the discussion of reaction energetics, we present in Fig. 6 a one-dimensional, Lennard-Jones energy diagram [39] representing the chemisorption and dissociation of a diatomic, AB, composed of two energy curves: (1) the interaction energy between adsorbate AB as a function of distance from the surface, and (2) the sum of the interaction energies of atom A and atom B as a function of the distance from the surface.

The UBI–QEP energy expression for interaction energy between AB and the metal surface is

\[ E_{AB} = Q_A (x_A^2 - 2x_A) + Q_B (x_B^2 - 2x_B) + D_{AB} (x_{AB}^2 - 2x_{AB}), \]  

which is subject to the UBI constraint

\[ x_A + x_B + x_{AB} = 1. \]

Since we wish to plot the minimum-energy path for the adsorption of AB in the Lennard-Jones diagram, we optimize the energy with respect to \( x_A \) and \( x_B \). The resultant expression is a one-dimensional energy equation that describes the minimum-energy path in terms of \( x_{AB} \) (Appendix D)

\[
E_{AB} = [Q_A Q_B / (Q_A + Q_B) + D_{AB}] x_{AB}^2 + [2Q_A Q_B / (Q_A + Q_B) - 2D_{AB}] x_{AB} \\
+ Q_A Q_B / (Q_A + Q_B) - Q_A - Q_B.
\]
It is clear that the AB bond index correlates uniquely with some measure of the distance to the surface along the minimum-energy path, such as the distance of the midpoint of the AB bond to the plane of the surface.

The other energy curve comprising the Lennard-Jones diagram is the sum of the atom-surface energies of non-interacting \((x_{AB} = 0)\) adatoms, A and B, as a function of atom-surface distance

\[
E_{A+B} = E_A + E_B = Q_A(x_A^2 - 2x_A) + Q_B(x_B^2 - 2x_B). \quad (4.6.1.4)
\]

No bond index conservation is imposed, since the adatoms are independent of each other.

Fig. 6 is the Lennard-Jones diagram showing the chemisorption and dissociation energy profiles of a typical diatomic, AB, as a function of distance from the surface, Eqs. (4.6.1.3) and (4.6.1.4). The Lennard-Jones maximum is the point at which the dissociation energy profile, Eq. (4.6.1.3), intersects the A + B chemisorption energy profile, Eq. (4.6.1.4) [39], and because everywhere along the \(E_{A+B}\) curve \(x_{AB} = 0\), the Lennard-Jones transition state AB bond index, \(x_{AB,LJ}\), is zero.

Putting the AB bond index to zero gives for the energy of the Lennard-Jones maximum:

\[
E_{AB,LJ} = Q_A Q_B / (Q_A + Q_B) - Q_A - Q_B. \quad (4.6.1.5)
\]

We convert this quantity into an expression for a reaction barrier by first realizing that any point along the reaction energy profile can be expressed in terms of the chemisorption energy minimum, \(E_{min}\), and an increment above the minimum, \(\Delta E_{AB}\):

\[
E_{AB} = E_{min} + \Delta E_{AB} = -D_{AB} - Q_{AB} + \Delta E_{AB}. \quad (4.6.1.6)
\]

Putting Eqs. (4.6.1.5) and (4.6.1.6) equal to each other gives

\[
\Delta E_{AB} = \Delta E_{AB,LJ} = D_{AB} + Q_A Q_B / (Q_A + Q_B) - Q_A - Q_B. \quad (4.6.1.7)
\]

in which \(\Delta E_{AB,LJ}\) is the Lennard-Jones activation barrier relative to adsorbed AB. From the thermodynamic cycle composed of AB desorption, AB gas-phase dissociation and A and B chemisorption, one obtains for the enthalpy of the surface reaction

\[
\Delta H = Q_A + D_{AB} - Q_A - Q_B \quad (4.6.1.8)
\]

so that the Lennard-Jones reaction barrier relative to surface adsorbed reactants is

\[
\Delta E^*_{AB,LJ} = \Delta H + Q_A Q_B / (Q_A + Q_B). \quad (4.6.1.9)
\]

This barrier is an overestimation. Since the AB dissociation energy profile is described by a quadratic expression, Eq. (4.6.1.3), there can be only one extremum, which corresponds to the AB chemisorption minimum. Therefore, on the dissociation side of the energy minimum, the energy simply increases with respect to decreasing \(x_{AB}\) until the end of the range is encountered. In the true transition state the AB bond distance is finite and therefore the AB bond index is greater than zero. This results in a transition state that has a lower energy than that of Eq. (4.6.1.5) and a barrier that is lower than that defined by Eqs. (4.6.1.7) and (4.6.1.9).

If we could determine the value of the AB bond index at the transition state, we could get the transition state energy from Eq. (4.6.1.3). Then the energy difference between the transition state and the chemisorbed state of AB would give the barrier height. The current framework of the UBI-QEP method does not, however, provide a means to determine this transition state bond index. In lieu of this, we proceed with the simplest possible interpolation, namely, taking the midpoint of the energy interval
given in Eqs. (4.6.1.7) and (4.6.1.9) as the point of dissociation. This gives for the activation barrier for AB dissociation:

\[ \Delta E_{AB}^* = \frac{1}{2}[\Delta H + Q_A Q_B / (Q_A + Q_B)]. \] (4.6.1.10)

This interpolation is tantamount to choosing a value for the AB bond index in the transition state, \( x_{AB,TS} \), that is dependent on the thermodynamic parameters of the system of interest. In Appendix D we present a set of equations that allows the computation of the transition state value of \( x_{AB} \) that is implied by \( \Delta E_{AB}^* \), Eq. (4.6.1.10). Table 4 gives values of \( x_{AB,TS} \) for several diatomic dissociations on metal surfaces. For comparison purposes the value of the AB bond index at the chemisorbed minimum, \( x_{AB,eq} \), is also given. The numbers under the heading of ‘%BER’ are the percent of the gas-phase AB bond energy that remains at the corresponding bond index (\( \%BER = \frac{100}{2}(x_{AB}^2 - 2x_{AB}) \)).

These dissociation reactions are projected to have late activation barriers. Adsorbates such as OH that may form islands via hydrogen bonding may undergo two dissociation reactions [68, 130]. In the first one, which corresponds to the zero coverage limit, an isolated adsorbate dissociates. In the second reaction the dissociation occurs for an adsorbate which is hydrogen bonded to another adsorbate. In the UBI-QEP method we account for these effects by modifying the \( Q_{AB} \) (and sometimes \( D_{AB} \)) parameter(s). For example, the two dissociations of OH on Pt(111) differ in that the second OH dissociation employs a \( Q_{AB} \) value that includes lateral interactions that are present when the adsorbates are hydrogen bonded [68, 130]. As seen in Table 4, this additional stabilization due to hydrogen bonding has a significant influence on the position of the activation barrier causing it to appear earlier in the reaction coordinate. Increasing the value of \( D_{AB} \) while holding all other parameters fixed has a similar effect. However, as a general rule, the atomic heats of adsorption increase with increasing \( D_{AB} \). A general trend discernible in these data is that the position of the transition state along the reaction coordinate seems to correlate more with the molecular heat of adsorption, \( Q_{AB} \), than with the AB dissociation energy or the barrier height. The cases examined that have the lowest transition state bond indices also are the ones with the more weakly bound reactant. The reader should keep in mind when considering the numeric values of \( x_{AB,TS} \) that the value of unity corresponds to the relaxed and desorbed (gas-phase) AB species, and values of \( x_{AB,TS} \) should be less than the equilibrium AB bond index in the chemisorbed state, \( x_{AB,eq} \).

### Table 4

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Surface</th>
<th>( D_{AB} )</th>
<th>( Q_{AB} )</th>
<th>( \Delta E_{AB}^* )</th>
<th>Adsorbed</th>
<th>( %BER )</th>
<th>TS</th>
<th>( %BER )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>Ag(111)</td>
<td>119</td>
<td>9</td>
<td>5</td>
<td>0.74</td>
<td>93</td>
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<tr>
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<td>0.58</td>
<td>82</td>
<td>0.11</td>
<td>21</td>
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<tr>
<td>OH(^b)</td>
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<td>59</td>
<td>25</td>
<td>0.58</td>
<td>82</td>
<td>0.27</td>
<td>47</td>
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<tr>
<td>N(_2)</td>
<td>Ni(111)</td>
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<td>94</td>
<td>0.06</td>
<td>12</td>
</tr>
<tr>
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<td>8</td>
<td>0.77</td>
<td>95</td>
<td>0.06</td>
<td>12</td>
</tr>
<tr>
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<td>9</td>
<td>8</td>
<td>0.75</td>
<td>94</td>
<td>0.05</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^a\) For notation and equations, see text and Appendix D. The values of the energetic parameters are from Table 1.

\(^b\) Lateral interactions important in island formation have been taken into account [38, 130].

\(^c\) Percent of bond energy remaining.
In principle, this analysis affords a way to determine geometric parameters of the transition state in reactions involving diatomics and simple polyatomic molecules. The determination of the transition state AB bond distance requires, in addition to $x_{AB,TS}$, the accurate determination of the gas-phase AB bond stretching potential, most likely from ab initio calculations, and therefore the mapping of $x_{AB}$ onto $r_{AB}$ is defined by Eqs. (3.4.1)-(3.4.4). The AB bond distance in the transition state is the value of $r_{AB}$ corresponding to $x_{AB} = x_{AB,TS}$. Due to the inverse exponential dependence of $x_{AB}$ on $r_{AB}$, when the AB bond index is small, large errors in $r_{AB}$ are produced by relatively small errors in $x_{AB}$, the accuracy of which depends in turn on the accuracy of the intrinsic activation barrier. For example, assuming a typical Morse potential for the AB stretching potential and $x_{AB,TS} = 0.05$, an error of 0.01 in the transition state AB bond index causes an error of 0.3 Å in the transition state AB distance, $r_{AB}$. A difference of 0.01 in $x_{AB,TS}$ is the level at which the transition state bond indices of O$_2$ and SO dissociation on Ag(1 1 1) differ. The thermodynamics of SO and O$_2$ are very similar with $Q_0$ and $D_{AB}$ values differing by about 1 and 6 kcal/mol, respectively. In general, the UBI-QEP estimates of transition state geometries can be used for qualitative purposes, e.g., to provide initial geometries in ab initio transition state calculations.

The recombination reaction is the reverse of a dissociation reaction and therefore the activation barrier is obtained from the corresponding barrier to dissociation and the conservation of energy:

$$\Delta E_{AB,rec}^* = \Delta H + \Delta E_{AB,dis}^*$$

and

$$\Delta H = \Delta E_{AB,f}^* - \Delta E_{AB,r}^*$$

in which the subscripts, $r$ and $f$, indicate reverse and forward, respectively.

4.6.2. Disproportionation

In a dissociation reaction a breaking bond allows the other bonds in the molecule to strengthen. The extreme of this occurs in a disproportionation reaction:

$$A + BC \rightarrow AB + C.$$  \hspace{1cm} (4.6.2.1)

We treat the reactants, $A + BC$, as a quasi-molecule, $A \cdot BC$, the $A \cdot B$ bond of which strengthens upon cleavage of the $B-C$ bond. In this picture the AB atom group is equivalent to A in our previous treatment of dissociation leading to Eq. (4.6.1.10), and C is equivalent to B in the dissociation treatment. By this direct analogy, the intrinsic activation barrier relative to surface adsorbed reactants for the disproportionation reaction is

$$\Delta E_{f,s}^* = 1/2[\Delta H + Q_{AB}Q_C/(Q_{AB} + Q_C)].$$  \hspace{1cm} (4.6.2.2)

The surface reaction enthalpy is

$$\Delta H = Q_A + Q_{BC} + D_{BC} - D_{AB} - Q_{AB} - Q_C.$$  \hspace{1cm} (4.6.2.3)

Again, the reverse activation barrier is obtained from the conservation of energy. The direction of the reaction is defined in such a way that $D_{BC} > D_{AB}$ (see below).

4.6.3. General features and discussion

The general equation for the intrinsic activation barrier of dissociation and disproportionation reactions may be written as follows:
Here, \( \alpha \) and \( \beta \) represent adsorbate species A, B, or AB, to be defined for each type of reaction. \( \Delta H \) is the reaction enthalpy as it occurs on the surface and is the sum of the enthalpies of the steps of the thermodynamic cycle:

\[
\Delta H_1 = \sum_r Q_r.
\]

\[
\Delta H_2 = \sum_p T_p - \sum_r T_r \quad \text{or} \quad \Delta H_2 = \sum_b D_b - \sum_f D_f.
\]

\[
\Delta H_3 = -\sum_p Q_p.
\]

\[
\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = \sum_r Q_r - \sum_p Q_p + \sum_b D_b - \sum_f D_f.
\]

The \( Q \) parameters in the above thermodynamic steps are the heats of adsorption of the respective reactants (\( r \)) or products (\( p \)) and \( T_i \) is the total gas-phase bond enthalpy for component \( i \) (\( r \) or \( p \)); i.e. \( T_i \) is the enthalpy required to dissociate the \( i \)th component into its constituent atoms. The \( D \) parameter represents the gas-phase enthalpy required to break the bond, and the sums over the \( D \) quantities in the alternate expression for \( \Delta H_2 \) are the sums over bonds broken, \( D_b \), and bonds formed, \( D_f \). The products and reactants should be labeled in such a way that \( \Delta H_2 \) above is greater than or equal to zero because within the UBI-QEP method, this quantity is always a type of dissociation energy (see below). The total surface reaction enthalpy to be used in Eq. (4.6.3.2) is the sum of the three enthalpies as indicated.

The above expressions for the intrinsic activation barriers give the barrier heights as measured from the surface adsorbed reactants and products. To obtain the dissociation barriers relative to gas-phase reactants one simply subtracts the heat of adsorption of the dissociating molecule, \( Q_{AB} \), from the barrier relative to surface adsorbed reactants:

\[
\Delta E_{i,e}^t = \Delta E_{i,s}^t - Q_{AB}.
\]
negative bond enthalpy is also excluded in the development of the expressions for the barriers [39]. For example, the Lennard-Jones energy diagram presumes a positive $D_{AB}$. In the case of the disproportionation reaction the requirement is that $\Delta H_2 = D_{BC} - D_{AB}$ is greater than zero because this quantity is the ‘dissociation energy’ of the quasi-molecule A--BC [39]. If this quantity is less than zero, one needs only reverse the disproportionation reaction and relabel the reactants and products to obtain the forward activation barriers. The reverse activation barrier is then obtained from the conservation of energy. It is not necessary to employ heats of adsorption, $Q$, from UBI–QEP formulas in the equations for the intrinsic activation barriers if the values of $Q$ are not accurate enough. Data from reliable experimental measurements of $Q$ can be used to obtain the UBI–QEP intrinsic reaction barriers.

4.7. Diffusion and apparent activation barriers

For many surface reactions, theory can project a small or even zero intrinsic activation barrier, but yet, these reactions, when studied experimentally, have non-zero apparent barriers. In general, it is important to know how the diffusion and intrinsic activation barriers combine to produce the apparent or observed barrier. The UBI–QEP method provides a way to estimate diffusion barriers for atoms and small polyatomic radicals which are usually the reactants in recombination and disproportionation reactions. Diffusion barriers of larger adspecies and closed-shell molecules are outside the scope of the method. Within the context of the UBI–QEP method, diffusion and intrinsic barriers have been combined to compose the apparent activation barrier [131], and below we present the proper analytic expressions.

We begin with the Arrhenius form of the apparent reaction rate constant

$$k_{app} = A \exp\left\{-\frac{\Delta E_{app}}{k_B T}\right\},$$

(4.7.1)

where $A$ is the Arrhenius pre-exponential factor, $\Delta E_{app}$ is the apparent activation barrier, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The dependence of $\ln(k_{app})$ on reciprocal temperature, $d \ln(k_{app})/d(1/T)$, defines the quantity $\Delta E_{app}$:

$$\Delta E_{app} = -k_B \left[d \ln(k_{app})/d(1/T)\right].$$

(4.7.2)

With this definition of the apparent activation barrier, all temperature dependent effects that influence the reaction rate are contributors to the apparent activation barrier. Certainly, reactant diffusion is a temperature dependent phenomenon and a contributor to the apparent activation barrier.

Diffusion constants or diffusivities of adsorbed species are similarly expected to exhibit Arrhenius behavior with respect to temperature

$$D = D_0 \exp\left\{-\frac{\Delta E_{diff}}{k_B T}\right\}.$$  

(4.7.3)

4.7.1. Atomic and molecular diffusion

Employing the UBI–QEP energy formulas, we construct an expression for the diffusion activation barrier for atoms and small polyatomic radicals (see Ref. [131] and Appendix E for details):

$$\Delta E_{diff,A} = \gamma_n Q_{nA} = Q_{nA}(n - 2)/(4n - 2).$$

(4.7.1.1)
Table 5
UBI-QEP diffusion barriers (kcal/mol) in the zero coverage limit on fcc(1 1 1) surfaces^a

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Metal</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>O</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>12</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>12</td>
<td>10</td>
<td>10</td>
<td>14</td>
<td>13</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>12</td>
<td>15</td>
<td>14</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>SCH\textsubscript{3}</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}O</td>
<td>6</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{2}</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{2}</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

^a Calculated as $Q_A/10$ from Eq. (4.7.1.1) for $n = 3$. The values of $Q_A$ obtained from Eq. (4.1.2) with $Q_{0A}$ values from Table 1.

The diffusion of these small molecular radicals is treated as quasi-atomic diffusion.

For most atoms and particularly for molecules, reliable experimental values of the diffusional barriers are rare. Various methods may give rather different estimates, as clearly illustrated in a recent comprehensive review by Seebauer and Allen [132]. Nevertheless, the UBI–QEP calculated barriers in Table 5 are in broad agreement with experiment [132]. For more specific comparisons, the reader is referred to Ref. [131].

4.7.2. Apparent activation barrier: diffusion versus intrinsic contributions

Now we consider recombination and disproportionation and the role of diffusion in these reactions. As far as diffusion is concerned, the mechanisms of these two types of reactions are similar. The details of this development are given in Ref. [131] and Appendix E. For the reaction

$$A + B \rightarrow \text{Products},$$

the apparent activation barrier is [131]:

$$\Delta E_{\text{app}}^* = \alpha \Delta E_{\text{int}}^* + (1 - \alpha) \Delta E_{\text{dif. A+B}}^*$$

(4.7.2.1)
where $0 \leq \alpha \leq 1$. $\Delta E_{\text{int}}^*$ is the intrinsic activation barrier and $\Delta E_{\text{diff.,} A+B}^*$ is the mutual diffusion barrier of A and B. The fact that the apparent activation barrier is given by this linear interpolation means that its value is bounded between the values of its two component barriers. The $\alpha$ parameter is itself a function of the diffusivity and intrinsic rate constant:

$$\alpha = D^i / (D^i + k_{\text{int}}),$$

(4.7.2.3)

where $D^i$ is the diffusivity of a precursor state (Ref. [131] and Appendix E) and $k_{\text{int}}$ is the intrinsic reaction rate constant. When $\Delta E_{\text{diff.,} A+B}^* \gg \Delta E_{\text{int}}^*$, then the diffusivity of the precursor state is small compared to the intrinsic rate constant, $D^i \ll k_{\text{int}}$, so that $\alpha \approx 0$ and the apparent activation barrier is essentially the mutual diffusion barrier. Conversely, when $\Delta E_{\text{int}}^* \gg \Delta E_{\text{diff.,} A+B}^*$, then $D^i \gg k_{\text{int}}$ and $\alpha \approx 1$ so that the apparent activation barrier is essentially the intrinsic activation barrier. When one of the component barriers of $\Delta E_{\text{app}}^*$ is much larger than the other, then the apparent activation barrier takes on the value of the larger of the two component barriers.

The mutual diffusion barrier, $\Delta E_{\text{diff.,} A+B}^*$, is ([131] and Appendix E):

$$\Delta E_{\text{diff.,} A+B}^* = \beta \Delta E_{\text{diff.,} A}^* + (1 - \beta) \Delta E_{\text{diff.,} B}^*$$

(4.7.2.4)

and

$$\beta = D_A / (D_A + D_B).$$

(4.7.2.5)

Again, $0 \leq \beta \leq 1$ so that the value of the mutual diffusion barrier is bounded by the values of its component barriers. When one component, say species A, is immobile, $\beta \approx 0$ and the $\Delta E_{\text{diff.,} A+B}^* \approx \Delta E_{\text{diff.,} B}^*$. In contrast to the apparent activation barrier, the mutual diffusion barrier takes on the value of the lesser of the two component barriers when one is much larger than the other.

We estimate the value of the mutual diffusion barrier as the harmonic average of the component barriers (Ref. [131] and Appendix E):

$$\Delta E_{\text{diff.,} A+B}^* \approx \frac{2 \Delta E_{\text{diff.,} A}^* \Delta E_{\text{diff.,} B}^*}{\Delta E_{\text{diff.,} A}^* + \Delta E_{\text{diff.,} B}^*}$$

(4.7.2.6)

where $\Delta E_{\text{diff.,} A}^*$ is the diffusion barrier of adatom A. Table 6 contains some sample mutual diffusion barriers for selected reactions on metal surfaces.

It is useful to develop some rules of thumb that provide guidance in determining when one should consider diffusion effects in the zero coverage limit. In all cases diffusion may be important in determining the apparent reaction rate when the intrinsic activation barrier is small or zero. Recalling Eq. (4.7.1.1), the diffusion barriers of atoms that have binding energies to fcc(111) surfaces in the range 60–120 kcal/mol will have diffusion barriers ranging from 6 to 12 kcal/mol. When the diffusion barriers of A and B are approximately equal to each other, then the mutual diffusion barrier, $\Delta E_{\text{diff.,} A+B}^*$, has also the same value. Small molecular radicals that adsorb via a single contact atom, although usually more strongly bound than small closed-shell molecules, are always less strongly bound than the bare contact atom. Therefore, their diffusion barriers are smaller than those of the bare contact atom. Assuming that the diffusion of small radicals such as NH$_2$, OH and SCH$_3$ in the zero coverage limit can be treated as quasi-atomic diffusion, their diffusion barriers on fcc(111) surfaces of late-series transition metals should be in the 3–5 kcal/mol range, with some exceptions. Small, closed-shell molecules such as water, methane, etc. are usually relatively weakly bound to the surface and should have rather low diffusion barriers (~1–2 kcal/mol). When the intrinsic activation barrier is competitive
4.8. Coverage effects on adsorption energetics

Since the above development considered no coadsorbates, it corresponds to the zero coverage limit. In treatment of finite coverages, the UBI–QEP method can account for both direct adsorbate–adsorbate interactions and indirect interactions through the metal surface [38,130]. If coverages are not too high, the indirect adsorbate–adsorbate interactions appear to be dominant [38] and the UBI–QEP method always predicts a decrease in the heat of adsorption of all admolecules affected. If the direct adsorbate–adsorbate interactions are considered, the heat of adsorption may sometimes increase with coverage [38].

The decrease in the heat of adsorption of a given molecule or atom predicted by the UBI–QEP method upon addition of a coadsorbate originates from the fact that the surface metal atoms interact with more than one adsorbate. Because of bond index conservation, a metal atom cannot interact with either adsorbate as strongly as it could if only one adsorbate were present. The strength of the two-center bonding interaction is described by the $Q_{0A}$ parameters determined in the absence of coadsorbates (see Table 1). The question is how the two-center bond strength of $M–A_m$ varies with increasing $m$.

Starting with an adatom in a hollow site, the UBI–QEP method allows one to express the atomic heat of adsorption of a single adatom in a specific environment of coadsorbates [38]. Employing the conservation of bond index to unity, one obtains all incremental changes in the two-center bond strengths due to coadsorption which can be combined into a multiplicative scaling factor that converts the zero coverage limit binding energy into a coverage dependent binding energy (the interested reader is referred to either Ref. [38] or Appendix F for the details of the derivation).

$$Q_{nA}(\theta) = \sigma Q_{nA}. \tag{4.8.1}$$

The ratio of the coverage dependent heat of adsorption to the zero coverage heat of adsorption is

$$\sigma = Q_{nA}(\theta)/Q_{nA} = (1/n) \sum_i (k_i/m_i)(2 - 1/m_i). \tag{4.8.2}$$

Table 6

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>$\Delta E_{\text{diff, A-B}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + O $\rightarrow$ CO</td>
<td>Cu</td>
<td>11</td>
</tr>
<tr>
<td>H + CH$_2$ $\rightarrow$ CH$_3$</td>
<td>Pd</td>
<td>7</td>
</tr>
<tr>
<td>H + H $\rightarrow$ H$_2$</td>
<td>Pt</td>
<td>6</td>
</tr>
<tr>
<td>O + O $\rightarrow$ O$_2$</td>
<td>Pt</td>
<td>9</td>
</tr>
<tr>
<td>O + CH$_3$ $\rightarrow$ CH$_3$O</td>
<td>Ni</td>
<td>7</td>
</tr>
<tr>
<td>N + O $\rightarrow$ NO</td>
<td>Ag</td>
<td>9</td>
</tr>
<tr>
<td>H + S(SH)$_3$ $\rightarrow$ HS(SH)$_3$</td>
<td>Au</td>
<td>5</td>
</tr>
</tbody>
</table>

*a From Eq. (E.20) of Appendix E. The values of $Q_A$ obtained from Eq. (4.1.2) with $Q_{0A}$ values from Table 1.

with or less than the diffusion barrier of the most strongly bound reactant, then the apparent activation barrier may contain a significant diffusion component. In the above numerical examples, diffusion may be important if $\Delta E_{\text{int}}^* \leq 10-12$ kcal/mol and one reactant is an atom, and $\Delta E_{\text{int}}^* \leq 5-6$ kcal/mol if both reactants are small molecular radicals. In general, each case is different, but this example illustrates how one might judge the relative importance of diffusion in the apparent activation barrier.
Table 7
Scale factors $\sigma$, for various coverages, $\theta$, on common crystal planes

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>fcc(111)</th>
<th>fcc(100) $n=4$</th>
<th>bcc(100) $n=5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000$^b$</td>
<td>1.000$^b$</td>
<td>1.000$^b$</td>
</tr>
<tr>
<td>1/4</td>
<td>1.000$^b$</td>
<td>1.000$^b$</td>
<td>1.000$^b$</td>
</tr>
<tr>
<td>2/7</td>
<td>1.000$^b$</td>
<td>0.938$^{b,c}$</td>
<td>0.950$^{b,c}$</td>
</tr>
<tr>
<td>1/3</td>
<td>1.000$^b$</td>
<td>0.875$^{b,c}$</td>
<td>0.900$^{b,c}$</td>
</tr>
<tr>
<td>2/5</td>
<td>0.917$^{b,c}$</td>
<td>0.812$^{b,c}$</td>
<td>0.850$^{b,c}$</td>
</tr>
<tr>
<td>3/7</td>
<td>0.852$^{b,d}$</td>
<td>0.734$^{b,c,e}$</td>
<td>0.788$^{b,c,e}$</td>
</tr>
<tr>
<td>4/9</td>
<td></td>
<td>0.734$^{b,c,e}$</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>0.833$^{b,c}$</td>
<td>0.750$^c$</td>
<td>0.800$^c$</td>
</tr>
<tr>
<td>3/5</td>
<td>0.704$^{b,d}$</td>
<td>0.594$^{c,e}$</td>
<td>0.675$^{c,e}$</td>
</tr>
<tr>
<td>2/3</td>
<td></td>
<td>0.594$^{c,e}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.556$^d$</td>
<td>0.438$^e$</td>
<td>0.555$^e$</td>
</tr>
</tbody>
</table>

$^a$The values of $\sigma$ have been calculated for local cluster $M_pA_q$ configurations that may or may not represent regular, repeating patterns. The cluster coverage, $\theta = q/p$, is the ratio of adatoms to metal atoms. $A$ is always in the $n$-fold hollow site, but the value of $m$ in $M_m-A$ varies. This table is reproduced from [38, Table 13].

$^b m=1.$

$^c m=2.$

$^d m=3.$

$^e m=4.$

The summation runs over the number of symmetry unique metal atoms of the binding site, i.e. metal atoms that bind to different numbers of adatoms. For the sake of this discussion, we group the metal atoms of the $n$-fold binding site into ‘local-symmetry types’ that are determined by the number of adatoms, $m_i$, to which they bind. So, the $m_i$ are the numbers of adatoms that bind to the binding site metal atom of local-symmetry type $i (i \leq n)$, and $k_i$ is the number of binding site metal atoms of the $i$th local-symmetry type, and $n$ is the number of metal atoms defining the binding site ($n = 3$ for an fcc(111) hollow, etc.) The scale factors are summarized in Table 7.

Consider some examples. Fig. 7 depicts a small cluster of adatoms on an fcc(100) surface. The central adatom is completely surrounded by other atoms in hollow sites. The four metal atoms comprising the central-most hollow site are each interacting with four adatoms. To discuss the effect of coverage, we introduce the parameter $\theta = \text{the number of adsorbate atoms, } A, \text{ per metal atom, } M$. From the point of view of the central adatom in Fig. 7, $\theta = 1$, since in the immediate neighborhood there is one adsorbate atom for every metal surface atom.

For the central adatom of Fig. 7, there is only one set of integers, $k_i$ and $m_i$, in the summation, Eq. (4.8.2), and the environment of this adatom is described by $n = 4$, $k_1 = 4$, and $m_1 = 4$ ($\theta = m/n = 1$). The heat of adsorption at this coverage is predicted to be $7/16 = 0.4375$ of the zero coverage limit value ($\sigma = 7/16$). Another arrangement, adatoms in a line, is shown in Fig. 8. This environment, excepting the end atoms, is described by $n = 4$ because the hollow sites are four-fold sites, $k_1 = 4$ because all four metal atoms of the four-fold site are involved in $M-A_m$ interactions (namely $M-A_2$) and $m_1 = 2$ because each of these metal atoms interacts with two A atoms. From Eq. (4.8.2), $\sigma = 3/4$. Taking $\theta = m/n$, this corresponds to a coverage of 0.5.
Fig. 7. Island of adatoms A (filled circles) on a metal (open circles) fcc(1 0 0) surface. The local environment of the central adatom (shown by dashed lines) corresponds to a coverage $\theta_A = 1$.

Fig. 8. Adatoms A in a line on a fcc(1 0 0) surface. The local environments of the non-end and end adatoms correspond to coverages of $\theta_A = 1/2$ and 1/3, respectively. See Fig. 7 for notations.

Care must be exercised here, because the local coverage $\theta = m/n$, where the $m$ and $n$ integers refer to the environment of a specific adatom, may not always correspond to the stoichiometric coverage, $\theta$, which is an average of all the local environments. In this latter situation $\bar{\theta}$ is the ratio of adsorbate atoms
to metal atoms in the limit of a line of atoms of infinite extent. For the adatoms at the ends of the line in Fig. 8, there are two sets of integers, \( k_i \) and \( m_i \), in the summation, Eq. (4.8.2): \( n = 4 \), \( m_1 = 2, k_1 = 2 \), and \( m_2 = 1, k_2 = 2 \), and for the heat of adsorption in this site, the scale factor, \( \sigma \), is 7/8. The coverage, \( \theta \), can be determined by reducing the line of adsorbate atoms to two, so that these two adsorbate atoms are coordinated to six metal atoms which give \( \theta = 1/3 \). In this way, any specific coverage dependent environment of like adatoms can be described by the set of integers \( \{n, k_i, m_i\} \) and the corresponding scale factor, \( \sigma \), determined from Eq. (4.8.2).

The same coverage, \( \theta \), on different crystal faces does not necessarily give the same value for the coverage dependent scale factor, \( \sigma \). We illustrate this by constructing adatom overlayers on fcc(111) and fcc(100) surfaces in which \( \theta = 1/3 \). Fig. 9 illustrates these overlayers. In the case of the fcc(111) surface, any given surface metal atom interacts with a single adatom \( (m = 1) \). However, on the fcc(100) plane, there are surface metal atoms that interact with two adatoms simultaneously \( (m = 2) \). The scale
factor, \( \sigma \), accounts for this, since it is a function of integers, \( n, m, \) and \( k_i \), which define these situations. The adatom environment on the (1 1 1) surface is characterized by: \( n = 3, m_1 = 1, k_1 = 1 \) so that \( \sigma = 1 \). For an adatom on the (1 0 0) surface: \( n = 4, m_1 = 1, k_1 = 2, m_2 = 2 \) and \( k_2 = 2 \) so that \( \sigma = 7/8 \). In Table 7 we have compiled a set of scale factors, \( \sigma \), for several coverages on common crystal planes.

The more general situation is the case of coadsorbates of two different atom types, A and B. Again, from the UBI constraint one obtains all incremental changes in two-center interactions and can combine them into one multiplicative scale factor. It is convenient to define a quantity that describes the binding energy of a single metal atom to a 'unit mesh' of adatoms \( A_m B_{m'} \) as \( Q_M(m, m') \):

\[
Q_M(m, m') = Q_{nB}(2 - 1/m')/n + m q^2/m' nd. \tag{4.8.3}
\]
\[
q = m'(Q_{nA} - Q_{nB}) + Q_{nB}. \tag{4.8.4}
\]
\[
d = m' Q_{nA} + m Q_{nB}. \tag{4.8.5}
\]

Either Ref. [38] or Appendix F describes the details of the derivation. The notation \( Q_M(m, m') \) emphasizes that this binding energy is a function of the numbers of different types of atoms, \( m \) and \( m' \). The strength of the individual metal–adatom interactions is

\[
Q_{0A}(\theta) = (Q_M(m, m') - Q_M(0, m'))/m = q^2/(m' nd). \tag{4.8.6a}
\]

Relabeling the atoms gives for adatoms of type B:

\[
Q_{0B}(\theta) = (Q_M(m, m') - Q_M(m, 0))/m' = q^2/(mnd), \quad \text{with } q \text{ properly relabeled.} \tag{4.8.6b}
\]

As in the homoatomic case, the new atomic heat of adsorption in the presence of coadsorbates is constructed by summing the two-center bond strengths. Fig. 10 depicts an fcc(1 0 0) surface in which a

Fig. 10. Island of adatoms of different types, A (checkered circles) and B (filled circles), on a fcc(1 0 0) surface (shown within dashed lines). The four metal atoms of the central hollow site equally share bonding with one A adatom and effectively with two B adatoms. See Fig. 7 for other notations.
Fig. 11. Island of adatoms of different types, A (checkered circles) and B (filled circles), on a fcc(100) surface (shown within dashed lines). Unlike Fig. 10, here the metal atoms of the central hollow site are not equivalent in their bonding with adatoms B. See text.

single adsorbate, A, is surrounded by four metal atoms which, in turn, interact with two adsorbates, B, of a different type.

The binding energy of the central adsorbate, A, can be obtained by summing the two-center bond strengths. All four of the metal atoms comprising the four-fold hollow interact with two B atoms and one A atom. For these metal atoms \( m = 1 \) and \( m' = 2 \). Each of the interactions between the metal atoms and atom A has a strength of \( Q_{0A}(\theta) = Q_{M}(1,2) - Q_{M}(0,2) \) (see Eq. (4.8.3)) so that the total binding energy of atom A, \( Q_A(\theta) \), in this environment is \( 4(Q_{M}(1,2) - Q_{M}(0,2)) \).

Fig. 11 depicts a more varied binding situation. Two of the B adatoms have been removed relative to Fig. 10 so that one of the four metal atoms interacts only with atom A with strength \( Q_{n}/n = 4 \); two metal atoms interact with A and one B atom each with strength \( Q_{0A}(\theta) = Q_{M}(1,1) - Q_{M}(0,1) \) for the M–A interaction; and the last metal atom of the four-fold hollow interacts with A and two B atoms with an M–A interaction strength of \( Q_{0A}(\theta) = Q_{M}(1,2) - Q_{M}(0,2) \). Summing these binding strengths gives the total heat of adsorption of the A atom:

\[
Q_A(\theta) = 7Q_{0A}/16 + 2(Q_{M}(1,1) - Q_{M}(0,1)) + Q_{M}(1,2) - Q_{M}(0,2).
\]  

The binding energies of the B adatoms can be obtained from an analogous process.

The effect of atomic coadsorption on molecular heats of adsorption of mono-coordinated admolecules is straightforward. The molecule will have a contact atom, and for a strongly bound molecular radical, the heat of adsorption, \( Q_{nA}(\theta) \), is modified by the presence of coadsorbates according to the above expressions. This \( Q_{nA}(\theta) \) is then used in Eq. (4.2.2.4) to determine \( Q_{AB} \). For a weakly bound molecule, the coverage dependent \( Q_{nA}(\theta) = Q_{0A}(\theta) \) corresponding to \( n = 1 \) substitutes for \( Q_{0A} \) in Eq. (4.2.1.3).

A general description of molecular coadsorption is largely beyond the scope of the UBI–QEP method. Firstly, polyatomics are typically much less strongly bound to the surface than are atoms so the electronic effects felt by neighboring admolecules through the metal surface are weaker. Secondly, polyatomics usually have a greater spatial extent which can lead to greater lateral interactions.
Although lateral interactions can be and have been included in the UBI–QEP method [38,130(a)], each type of molecular adsorbate is different and these modifications need to be made on an individual basis.

The effect of coverage of some polyatomic fragments can be treated efficiently within the UBI–QEP method. Small, strongly bound molecular radicals, such as CH₂, NH, SH, etc. are realistically treated as pseudo-atomic species. As described above, such strongly bound molecular radicals tend to behave like atoms, although consideration of lateral interactions is critical for adsorbates that are expected to interact with each other, such as OH [130(a)] and CNH₂ [130(b)] which form dimers and even islands through hydrogen bonding. In such cases the heat of adsorption, \( Q_{AB} \), where A is the contact atom and B is a group of atoms representing the molecular fragment minus the contact atom, takes the place of \( Q_{0A} \) in the equations of this section, and \( Q_{0AB} \) is constructed by dividing \( Q_{AB} \) by \( (2 - 1/n) \) where \( n \) is the number of metal atoms in the binding site.

4.9. Accuracy of UBI–QEP projections

The justification of a theoretical method and its underlying assumptions is the validity of the overall conceptual picture that one obtains from the method. The UBI–QEP method is designed for the calculation of molecular heats of adsorption and activation barriers for reactions on metal surfaces. From the practical point of view, it is important to foresee areas where the method is most and least accurate and to identify the sources of errors. Recall that the initial UBI–QEP parameters are atomic binding energies, which are either measured experimentally or estimated theoretically. In principle, the atomic binding energies depend on the number of metal atoms to which the adatom coordinates, so the energies may be different for different surfaces, and therefore, should be measured independently. If they are inaccurate, the resulting UBI–QEP energetics are skewed. Fortunately, the error in the atomic binding energy causes significantly less error in the molecular adsorption energy, and thus, for the reaction enthalpy and activation barrier. There may be other sources of uncontrolled errors. For example, when the surface reconstructs during a reaction, the energetics should be calculated with parameters that correspond to the reconstructed surface (i.e. parameters which account for the reconstruction), which may be different from those of the unreconstructed surface. Due to the scarcity of such quantities, close-packed surfaces, which are much less prone to reconstruction than open surfaces, are most amenable to the UBI–QEP treatment. This is believed to be a minor limitation because practical metal catalysis typically are (supported) polycrystalline powders having close-packed structure.

Errors may further accumulate while treating coverage effects on the surface energetics. The UBI–QEP formalism is best defined for the zero coverage limit and well defined for selected higher coverages. Although the treatment of bimetallic surfaces involves additional approximations and assumptions, we expect the bimetallic treatment to be of similar accuracy. Below we give a representative collection of comparisons between experimental and the UBI–QEP values of \( Q \) and \( \Delta E' \) for appropriate cases corresponding to: (a) good experimental values of \( Q_A \), (b) unimetallic close-packed surfaces, and (c) low coverages (the energetics of higher coverages is discussed in Section 4.8).

4.9.1. Zero coverage limit

4.9.1.1. Heats of adsorption

The UBI–QEP method usually makes projections of heats of adsorption that agree with reliable experimental data to within 1–2 kcal/mol. The agreement between the heats of adsorption obtained
Table 8
UBI–QEP molecular heats of adsorption, $Q$ (kcal/mol)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Metal surface</th>
<th>Site</th>
<th>Mode</th>
<th>Eq.</th>
<th>Calc. $^a$</th>
<th>Exp.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>Ag(1 1 1)</td>
<td>Ontop</td>
<td>Mono O</td>
<td>(4.2.1.4)</td>
<td>9.5</td>
<td>10.5</td>
<td>[265]</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>Rh(1 1 1)</td>
<td>Ontop</td>
<td>Mono O</td>
<td>(4.2.1.4)</td>
<td>14.5</td>
<td>14</td>
<td>[266]</td>
</tr>
<tr>
<td>OH</td>
<td>Pt(1 1 1)</td>
<td>Hollow</td>
<td>Mono O</td>
<td>(4.2.2.4)</td>
<td>59</td>
<td>60</td>
<td>[267,268]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Pt(1 1 1)</td>
<td>Ontop</td>
<td>Mono O</td>
<td>(4.2.1.4)</td>
<td>10.1</td>
<td>9.6</td>
<td>[265]</td>
</tr>
<tr>
<td>CO</td>
<td>Ni(1 1 1)</td>
<td>Ontop</td>
<td>Mono C</td>
<td>(4.2.1.4)</td>
<td>29</td>
<td>27</td>
<td>[255]</td>
</tr>
<tr>
<td>NO</td>
<td>Pd(1 1 1)</td>
<td>Bridge</td>
<td>Mono N</td>
<td>(4.2.1.4)</td>
<td>32</td>
<td>31</td>
<td>[255]</td>
</tr>
<tr>
<td>NO</td>
<td>Pt(1 1 1)</td>
<td>Bridge</td>
<td>Mono N</td>
<td>(4.2.1.4)</td>
<td>26</td>
<td>27</td>
<td>[255]</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Pt(1 1 1)</td>
<td>Bridge</td>
<td>Di O</td>
<td>(4.2.1.7)</td>
<td>11</td>
<td>9</td>
<td>[269]</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Pt(1 1 1)</td>
<td>Bridge</td>
<td>Di N</td>
<td>(4.2.1.7)</td>
<td>11</td>
<td>9</td>
<td>[271]</td>
</tr>
<tr>
<td>SCH$_3$</td>
<td>Au(1 1 1)</td>
<td>Hollow</td>
<td>Mono S</td>
<td>(4.2.2.4)</td>
<td>44</td>
<td>44</td>
<td>[270]</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Ni(1 1 1)</td>
<td>Ontop</td>
<td>Mono N</td>
<td>(4.2.1.4)</td>
<td>18</td>
<td>20</td>
<td>[272]</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Pt(1 1 1)</td>
<td>Ontop</td>
<td>Mono N</td>
<td>(4.2.1.4)</td>
<td>11–14</td>
<td>12</td>
<td>[256]</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>Pt(1 1 1)</td>
<td>Hollow</td>
<td>Mono N</td>
<td>(4.2.2.4)</td>
<td>39–47</td>
<td>&gt;42</td>
<td>[273]</td>
</tr>
<tr>
<td>NH</td>
<td>Pt(1 1 1)</td>
<td>Hollow</td>
<td>Mono N</td>
<td>(4.2.2.4)</td>
<td>71</td>
<td>71–74</td>
<td>[273]</td>
</tr>
<tr>
<td>HCOOH</td>
<td>Au(1 1 0)</td>
<td>Bridge</td>
<td>Di O</td>
<td>(4.3.2.3.1)</td>
<td>12</td>
<td>13</td>
<td>[274]</td>
</tr>
</tbody>
</table>

$^a$Zero coverage limit binding energies. The values of $Q_A$ obtained from Eq. (4.1.2) with $Q_{0A}$ values from Table 1.

Table 9
UBI–QEP intrinsic activation barriers (kcal/mol) for selected reactions on fcc(1 1 1) surfaces

<table>
<thead>
<tr>
<th>Reaction/metal</th>
<th>$\Delta E_{\text{calc}}^a$</th>
<th>$\Delta E_{\text{exp}}^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O $\rightarrow$ 2OH/Pt</td>
<td>11</td>
<td>10</td>
<td>[268]</td>
</tr>
<tr>
<td>H + O $\rightarrow$ OH/Pt</td>
<td>10</td>
<td>&lt;13</td>
<td>[268]</td>
</tr>
<tr>
<td>H + OH $\rightarrow$ H$_2$O/Pt</td>
<td>11</td>
<td>16 ± 5</td>
<td>[268]</td>
</tr>
<tr>
<td>CH$_2$O + H $\rightarrow$ CH$_3$OH/Rh</td>
<td>13</td>
<td>13</td>
<td>[266]</td>
</tr>
<tr>
<td>CH$_2$ $\rightarrow$ CH$_3$ + H/Pt</td>
<td>18</td>
<td>18</td>
<td>[59]</td>
</tr>
<tr>
<td>C$_2$H$_4$ $\rightarrow$ C$_2$H$_5$ + H/Pt</td>
<td>13</td>
<td>16</td>
<td>[59]</td>
</tr>
<tr>
<td>CO + O $\rightarrow$ CO$_2$/Rh</td>
<td>24</td>
<td>27</td>
<td>[275]</td>
</tr>
<tr>
<td>CO + O $\rightarrow$ CO$_2$/Pt</td>
<td>23</td>
<td>25</td>
<td>[276]</td>
</tr>
<tr>
<td>NO + N $\rightarrow$ N$_2$O/Rh</td>
<td>22</td>
<td>21</td>
<td>[277]</td>
</tr>
<tr>
<td>NO + N $\rightarrow$ N$_2$O/Pt</td>
<td>22</td>
<td>20</td>
<td>[278]</td>
</tr>
</tbody>
</table>

$^a$Zero coverage limit values. The values of $Q_A$ obtained from Eq. (4.1.2) with $Q_{0A}$ values from Table 1.

from the UBI–QEP method and experimental data has been seen in Table 8 for a variety of adsorbates. Usually the UBI–QEP values should be compared to experimental ones at low coverage (the zero coverage limit), although coverage effects can be taken into account [38]. Even at low coverages, some adsorbates form islands creating a situation of locally high coverage. Although the standard UBI–QEP method does not account for direct adsorbate–adsorbate interactions, or lateral interactions, these effects can be incorporated into the model [38,130]. For example, when lateral interactions such as hydrogen bonds were taken into account, the UBI–QEP projections for the OH molecular radical came into agreement with experimental data [38,130]. We do not know of any case in which the UBI–QEP
method fails to predict heats of adsorption at this level of accuracy when compared with reliable experimental results corresponding to the zero coverage limit.

4.9.1.2. Activation barriers

Reliable experimental data on activation barriers are more scarce than those for heats of adsorption. Some representative examples are shown in Table 9. It is evident that the calculated UBI–QEP values are usually accurate to within a few kcal/mol.

5. Molecular dynamics simulations using a modified UBI–QEP potential function

So far we have developed the UBI–QEP method for projections of heats of adsorption and intrinsic and diffusion activation barriers. Now we extend this method to the calculation of the Arrhenius pre-exponential factor to complete the specification of the reaction rate constant. The importance of this extension is obviously to provide a method of obtaining the full Arrhenius rate constant so that kinetic models of reaction mechanisms can be constructed.

Since the pre-exponential is a high temperature limiting value of the reaction rate constant, it should be largely insensitive to the part of the potential energy surface (PES) responsible for low temperature phenomena. In other words, as long as the overall energetics of the reaction are adequately represented, one should not expect the pre-exponential factor to be sensitive to the part of the PES that is responsible for the details of the adsorbate structure in its preferred binding site. These details simply do not have much influence on the high temperature dynamics. In the high temperature limit, the reaction rate constant depends on the coarse features of the potential energy surface and not the finer details, and therefore, it makes no sense to invest computational effort on that part of the PES responsible for such attributes as the precise orientation of an admolecule in its equilibrium position. The suitability of the UBI–QEP potential energy function for this level of description is demonstrated by its success at predicting reaction energetics.

Within the UBI–QEP method, the potential energy hypersurface of the AB system is described by the many-body potential

\[ E_{AB} = Q_A(x_A^2 - 2x_A) + Q_B(x_B^2 - 2x_B) + D_{AB}(x_{AB}^2 - 2x_{AB}) \]  

(5.1)

which is the sum of the relevant two-body quasi-spherical interactions. Here the effective contribution of each two-body interaction is determined by the total energy minimization under the UBI normalization constraint, which for the reactant state is

\[ x_A + x_B + x_{AB} = 1 \]  

(5.2)

and holds up to the dissociation point, after which the fragments, A and B, behave independently. Therefore, after dissociation, their total bond index, \( x_A \) and \( x_B \), will vary (increase) until it reaches the maximum value of two, which corresponds to \( x_A = x_B = 1 \) in the A and B equilibrium states. To accommodate both the reactant and product states, the UBI constraint, Eq. (5.2), will be modified.

Thus, the UBI–QEP potential energy hypersurface is effectively the minimum energy profile up to the dissociation point along the reaction coordinate, where local minima correspond to the reactants and products in their thermodynamically equilibrium chemisorbed states. As we have seen, the greatest advantage of the UBI–QEP method is that the energies of stationary points can be simply and reliably
obtained without knowing details of the interaction potentials and adsorbate geometries. However, even for this (static) energy hypersurface, calculations of the energies of various non-stationary points may become cumbersome and inaccurate.

Obviously, there may be different ways to modify the static UBI–QEP potential functions to describe dynamic situations. The major physical requirements for a trial potential function are that it should have the correct asymptotic behavior and describe the smooth dissociation of one molecule, AB, into two independent A and B fragments. Of course, for the sake of simplicity and computational expense, it would be desirable to reduce the number of additional terms and parameters to a minimum. Below we describe the way in which we have modified the UBI–QEP method.

First, during the vibrations of a molecule, AB, the bond index, \( x_{AB} \), takes on values that are smaller and larger than unity, corresponding to the A–B bond distances being larger or smaller than the equilibrium value. Previously all bond indices were required to be non-negative and less than or equal to unity. In our modification of the bond index normalization constraint, we allow for bond indices greater than unity and even negative values of interaction indices, \( Z_A \) and \( Z_B \) (defined and discussed below), which are analogous to atom-surface bond indices when they have non-negative values. We construct the \( Z_A \) and \( Z_B \) functions in such a way as to allow for both attractive and repulsive contributions from the adatom–surface interactions, which provides further variational flexibility. (Recall that the UBI–QEP potentials explicitly are never repulsive; the repulsive contributions are introduced indirectly through the UBI constraint.)

Second, in order to treat the AB vibrations explicitly, the potential energy function should reduce to the gas-phase AB vibrational potential function at large distances from the surface. This imposes a requirement on the analytic form of the PES, and the adatom–surface interaction potential can no longer be assumed to be a function of a single effective A-surface distance.

Third, some UBI–QEP parameters, particularly the atomic chemisorption energies, \( Q_A \), which were discrete and had fixed numerical values for chemisorption states, must now be cast as a continuous function of the appropriate coordinates.

Consider the surface dissociation reaction

\[
AB(\text{ad}) \rightarrow A(\text{ad}) + B(\text{ad}).
\]  

(5.3)

In the static situation we had the UBI–QEP equations (4.2.1.6) or (5.2) which we imposed as a constraint in the energy minimization procedure. The UBI normalization describes the bond index normalization in the reactant state. Now, we modify the bond index normalization so that it describes the bond index of both the reactant and product states [133–135]:

\[
\beta(Z_A + Z_B) + x_{AB} = N \quad (5.4)
\]

and

\[
N = 1 + \exp\{-\gamma \Delta^i\}, \quad x_{AB} < 1, \quad N = 1, \quad x_{AB} \geq 1. \quad (5.5)
\]

The \( \beta, \gamma \) and \( i \) are quantities that are determined within the UBI–QEP framework (Appendix G). Now, \( Z_A \) and \( Z_B \) are interaction indices and functions of the in-plane coordinates only (the dependence on the perpendicular distance above the surface is introduced via the energetic parameters). Unlike bond indices they can be negative as well as non-negative. The non-negative values correspond to the bond indices that atoms A and B would have if the atoms were on the minimum energy surface, and this is certainly the case in the dissociation limit. The \( x_{AB} \) variable is the usual AB bond index which we normally take to be a one-term exponential.
The $\Delta$ function is

$$\Delta = x_{AB}/(1 - x_{AB}), \quad x_{AB} < 1. \quad \Delta \text{ is infinite for } x_{AB} \geq 1. \quad (5.6)$$

We have found that $\ell = 2$ is often a good choice [133–135] for the exponent of $\Delta$ in Eq. (5.5).

The equation for the energy surface is

$$V = Q_A(Z_A^2 - 2Z_A) + Q_B(Z_B^2 - 2Z_B) + D_{AB}(x_{AB}^2 - 2x_{AB}). \quad (5.7)$$

The Morse potentials, $Q_A$, are dynamic Morse potentials [110,111] and contain the information about the topology of the surface, and are functions of the distance coordinate perpendicular to the surface:

$$Q_A = -q_A(W_A^2 - 2W_A), \quad (5.8)$$

where $W_A$ is a one-term bond index-type quantity and is a function of the distance above the surface. The dynamic Morse potentials are determined by fitting the $q_A$ function to UBI-QEP atomic binding energies (Appendix G).

Minimization of the energy with respect to $Z_A$ and $Z_B$ subject to the bond index normalization gives (Appendix G):

$$Z_A = ((q_A - q_B) + q_B(N - Z_{AB})/\beta)/(q_A + q_B), \quad (5.9)$$

$$Z_B = ((q_B - q_A) + q_A(N - Z_{AB})/\beta)/(q_A + q_B).$$

We emphasize that the potential function, Eq. (5.7), while it employs dynamic Morse potentials to represent the dependence of the energy on the perpendicular distance, retains the general quadratic exponential potentials, which are the terms involving $Z_A$ and $Z_B$. For example, the potential energy term, $Q_A(Z_A^2 - 2Z_A)$, is not a Morse potential but a rather complex expression after making substitutions for $Z_A$ from Eq. (5.9) and $q_A$ and $q_B$ from Eq. (G.5). The retention of the quadratic exponential potential is a strength of the method. In Section 9.8 we present results of molecular dynamics simulations of various diatomic dissociation reactions employing the above potential energy function.

6. UBI–QEP energetics on bimetallic surfaces

The UBI–QEP method has been extended to treat heats of adsorption and reaction energetics on bimetallic surfaces. The method presumes a specific arrangement of the different types of metal surface atoms and makes projections regarding the heats of adsorption and activation barriers. The fact that the UBI–QEP method does not select the preferred structure of the alloy surface is not an impediment because it is easy to test all possible arrangements of surface atoms, particularly when the method is computerized, in order to determine what differences there might be in chemical reactivity. In this section we summarize the UBI–QEP treatment of atomic chemisorption on bimetallic surfaces with some comments on molecular chemisorption. The cumbersome formalism is left to Appendix C. To obtain activation barriers for reactions on bimetallic surfaces, one simply uses the relevant bimetallic heats of adsorption in the equations for the activation barriers (Section 4).

6.1. Atomic chemisorption

Consider atomic adsorption within a bimetallic unit mesh, $M_iM'_j$, composed of $l$ atoms $M$ and $l'$ atoms $M'$ as shown in Fig. 12.
As shown in Appendix C, in the atomic binding site, $M_1M'_2-A$, the $M_1-A$ interactions are equivalent as are the $M'_2-A$ interactions, so the energy expression for atomic adsorption can be written as

$$E = lQ_{0A}(x_1^2 - 2x_1) + l'Q'_{0A}(x_2^2 - 2x_2).$$

where $x_1$ indicates a two-center bond index between adatom $A$ and a metal atom, $M$, of type 1. The primed quantities refer to the metal atom, $M'$, of type 2, and, the $l$ and $l'$ coefficients account for the symmetry of the interactions. Minimization of the atomic binding energy under the unity bond index constraint gives (Appendix C):

$$Q_A = \frac{l[l'Q_{0A} + (1 - l')Q'_{0A}]^2}{l'(l'Q_{0A} + lQ'_{0A})} + Q_{0A}(2 - 1/l').$$

At this point it is instructive to see some actual atomic binding energies on bimetallic surfaces. Table 10 contains the heat of adsorption of atomic oxygen on bimetallic surfaces of Pt mixed with Cu, Pd, Ni, Ag and Au. The three-fold hollow site is assumed ($l + l' = 3$), and we consider both types of binding sites, in which the ratios of platinum to the other metal, Pt/M, are 2 and 1/2. For comparison, the heats of adsorption of oxygen on the pure metal surfaces, Pt(111) and M(111), are also given. From the data in Table 10 one sees that the atomic heat of adsorption varies between the two extremes of pure metal 1 and pure metal 2 as an essentially linear function of the number of metal atoms of the second type.

6.2. Molecular adsorption

Now let us turn to molecular chemisorption. Strongly bound radicals on bimetallic surfaces are treated similar to strongly bound radicals on unimetallic surfaces; the strong binding formula, Eq. (4.2.2.4), and the formulas for activation barriers (Section 4.6) simply use the appropriate bimetallic atomic heats of adsorption, Eq. (6.1.2). However, the weak binding formulas for erect and horizontal chemisorption on bimetallic surfaces are significantly more complex. These formulas are given in Appendix C.

Despite the rapidly growing knowledge of physical and chemical properties of bimetallic surfaces [136–139], the unit mesh compositions and the adsorption energetics are usually unknown or, at best,
Table 10

UBI-QEP atomic heats of adsorption, \( Q_0 \) (kcal/mol) of oxygen on fcc(111) Pt/M bimetallic surfaces

<table>
<thead>
<tr>
<th>Composition of three-fold hollow site</th>
<th>M</th>
<th>Pt(_3)(^b)</th>
<th>Pt(_2)M(_1)</th>
<th>Pt(_1)M(_2)</th>
<th>M(_3)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>85</td>
<td>91.7</td>
<td>97.6</td>
<td>103.0</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>85</td>
<td>85.7</td>
<td>86.5</td>
<td>87.2</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>85</td>
<td>96.5</td>
<td>106.7</td>
<td>115.0</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>85</td>
<td>83.4</td>
<td>81.7</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>85</td>
<td>81.9</td>
<td>78.6</td>
<td>75.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Calculated from Eq. (6.2) for \( l = l' = 3 \). The values \( Q_{0A} \) are taken from Table 1.

\(^b\)Experimental values of \( Q_0 \) on Pt and other metals are taken from Ref. [39].

far from certain. For this reason, the UBI-QEP formulas in Appendix C illustrate the potential to be used in the future when the appropriate experimental data become available.

7. UBI-model: a computer program for modeling surface reaction energetics

The UBI-QEP method is now fully automated in a user-friendly FORTRAN-77 program complete with databases of \( Q_{0A} \) and \( D_{AB} \) values [76]. The program allows the user several levels of control. The most automated level relieves the user of specifying anything beyond the reaction and the metal surface while the least automated level allows the user the freedom to specify everything from the chemisorption modes and binding sites of all participating adsorbates to special values of the \( Q_{0A} \) and \( D_{AB} \) parameters. Running in an automation mode, the program decides which binding site and coordination mode to employ for a particular adsorbate based on a set of automated rules. In the case that two or more chemisorption modes and binding sites are close in energy, the program performs calculations with all candidate binding sites and modes.

The input to the program is particularly simple. The program reads chemical reactions essentially the same way that chemists write them. The default output of the UBI-model is composed of the enthalpy for the surface reaction and the forward and reverse activation barriers. All intermediate information can, however, be displayed.

The hardware demands of the program are modest. It should run on any computer with a FORTRAN compiler that supports FORTRAN-77. Execution time is not a concern. Although the precise run-times are compiler specific, the program will compute the energetics of more than 200 reactions on a 486-class personal computer in just a few seconds. It uses a minimum of memory (\(< 0.5 \text{ Mb}\)).

8. Combined ab initio and UBI-QEP modeling

8.1. Characteristics of ab initio surface chemistry modeling

The microscopic picture of chemical processes on metal surfaces can be understood only through quantum mechanical calculations of sufficient quality. Features such as adsorbate geometries in
chemisorbed and transition state, and electronic details of orbital interactions are difficult or impossible to obtain from experimental data. Only quantum mechanical modeling is capable of providing this information. Whitten and Yang [35] have recently reviewed the present situation with regard to ab initio modeling of chemisorption and surface reactions on metal surfaces.

An example of the microscopic-level understanding that can come only through high quality ab initio calculations is the new paradigm of the surface chemical bond on transition metals. As one goes across the periodic table in the transition metal series, an apparent difference between metal atoms is the number of d electrons. (Of course there are many other differences, such as the relative stability of the s bands, but they are less visible.) So, it seems natural to look to the d orbital interactions for explanations of the transition metal surface chemistry. Accordingly, early approximate quantum mechanical calculations and symmetry analyses based on comparisons with ligand complexes led to the paradigm of surface-adsorbate interactions being dominated by the metal d orbitals [30]. The high quality quantum mechanical calculations that are possible today on adsorbed atoms and small molecules give a very different picture. Modern calculations reveal the new paradigm of the surface bond that is dominated by interactions with metal atom s orbitals and to some extent p orbitals with the d orbitals of the metals playing a minor role [31,34,35]. Also, as clearly shown in the review by Whitten and Yang [35], the metal s and p orbitals of metal surfaces can satisfy symmetry requirements that these orbitals of single metal atoms in ligand complexes cannot. Therefore, the extrapolation of results relevant to bonding in metal ligand complexes to bonding on metal surfaces is not a valid procedure. Nevertheless, many chemists are still reluctant to give up the old paradigm that metal surface chemistry is a result of interactions involving predominantly metal d orbitals ignoring the fact that modern, high quality quantum mechanical calculations reject it.

To date only a small number of chemisorbed non-metal atoms and molecules have been studied with ab initio methods. These include O, N, C, H, S atomic adsorbates and CO, OH, SH, H2O, SCH3, CH3, CH3O and benzene [35], SO, SO2, SO3 [75], H2SO4 [140], and a small number of ions such as H+, H–, OH+ and OH–, halides, sulfite and sulfate [141–143]. In their exhaustive review, Whitten and Yang cite five bona fide reaction studies conducted at the ab initio level: dissociations of CO, H2, CH4, oxidation of NH3 and recombination of H + CH3. Presently there are no more complex systems of reactions treated at the ab initio level in the literature.

In ab initio calculations of surface phenomena there are two computational aspects that strongly affect the quality of the computed result: (a) the level of ab initio treatment which includes the completeness of basis sets employed and the level at which electron correlation is treated; and (b) the quality of the model of the metal surface employed which usually translates into the size of the cluster of metal atoms used to represent the surface of the bulk. For a given level of ab initio treatment, for example, Hartree-Fock + MP2 correlation, it is extremely important to know how well converged the computed results are with respect to the size of the model of the metal surface. Without this knowledge the reliability of the ab initio quantities computed cannot be judged. Convergence studies of this kind exist in the literature in which binding energies and adsorbate geometries have been determined with ab initio methods on cluster models of metal surfaces of increasing size [142–146]. The Siegbahn group has demonstrated [144] that stable (to within ~5 kcal/mol) binding energies of neutral adsorbates with respect to the size of the metal cluster can be obtained with relatively small cluster models of metal surfaces when the electronic state of the metal cluster is a properly prepared bonding state. Although stable or converged binding energies with respect to cluster size can be obtained, the absolute accuracy depends on the level of sophistication of the ab initio method employed. It is important to remember
that a stable or converged binding energy with respect to cluster size does not automatically imply that it is an accurate value.

Binding energies of closed-shell adsorbates to metal surfaces are often less demanding of ab initio treatments than open-shell adsorbates. One reason for this is that open-shell adsorbates have unpaired electrons that form singlet-coupled pairs involving electrons from the metal surface which must be separated if the adsorbate is directly dissociated from the surface. To avoid the separation of singlet-coupled electron pairs in atomic binding energy calculations, Sellers [147] has employed thermodynamic cycles in conjunction with ab initio calculations. Many polyatomic ions are closed-shell species. Sellers et al. [142] have shown with HF + MP2 calculations that the closed-shell nature of the polyatomic ions is responsible for the fact that the correlation energy is a minor contributor to the binding energy. However, the requirement that a model of the metal surface must respond to the electric charge of the ion places additional demands on the metal cluster. In cases in which the model of the surface must delocalize a net electric charge, positive or negative, as in cases such as adsorption of H⁺, H⁻, OH⁺, etc., then, in addition to a strict size demand, there is also a shape demand with the more hemispherically shaped cluster models giving more physically reasonable charge distributions over the metal atoms [142].

In summary, the quality of ab initio chemisorption and catalysis modeling results depends on several features: the quality of basis sets employed, the quality of the description of the metal surface, the level of quantum mechanical theory applied, whether or not the adsorbates are ions, etc. The vast majority of ab initio binding energy calculations in the literature are of insufficient quality to be of quantitative accuracy (within 1–3 kcal/mol). Although modern computational technology has made great gains in the last decade, many important and complex systems of chemical reactions are presently out of the scope of applicability of modern quantum chemistry.

8.2. The synergism of the UBI–QEP and ab initio methods

Several aspects of the UBI–QEP and ab initio methods are complementary to each other. Due to the bond index space optimization technique, the UBI–QEP method does not require knowledge of the details of the system geometry. This type of information is best obtained from ab initio calculations. It has long been known that gas-phase molecular geometries and force constants converge more rapidly with respect to basis set size and level of ab initio treatment than do binding energies. This is also true in the cluster modeling of adsorbate–surface chemistry [29,144,146]. On the basis of results of ab initio metal cluster calculations, Bauschlicher [146] pointed out in the mid-1980s that adsorbate geometries and force constants converge more rapidly with respect to the size of the cluster model of the metal surface than do adsorbate binding energies when the electronic ground state of the metal cluster is used. This is now widely accepted as a feature of ab initio calculations. Because different approximations are made in the derivation of the UBI–QEP binding energy formulas, the UBI–QEP method should not be used to distinguish between binding sites and coordination modes that are close in energy. Although, ab initio predictions of binding energies, or binding energy differences, that are accurate to the 1–3 kcal/mol level are difficult [146], ab initio calculations can often be useful in determining which binding site and coordination mode is preferred in situations in which the UBI–QEP would not give reliable results.

We have employed ab initio and UBI–QEP calculations in this synergistic way in our studies of sulfur oxide chemistry on metal surfaces [75]. In these studies ab initio calculations in which the
adsorbate geometries were relaxed were used to determine trends in preferred binding sites and coordination modes of SO, SO$_2$ and SO$_3$ on Ag, Au and Pd surfaces. This information was then used in our UBI–QEP modeling of the sulfur oxide chemistry [74]. This work and others are discussed in Section 9.

9. Selected applications of the UBI–QEP method

Systems of reactions on transition metal surfaces which have been studied employing the UBI–QEP method are very diverse [67–75,130,131,148,149]. Some of these studies have already been discussed in the previous reviews [38,39], but most of them are later works, in particular the Fischer–Tropsch synthesis [70], the methanol synthesis by both conversion of methane [67] and conversion of CO and CO$_2$ [69], the synthesis and decomposition of ammonia [71], oxygen-assisted X–H bond cleavage [149], formation and reaction of allylic species [73], the hydrogen peroxide synthesis [68], decomposition and reduction of NO species [72] and chemistry of sulfur oxides [74]. These works represent applications of the UBI–QEP method to chemically important and complex processes which involve sets of reactions containing tens and even hundreds of elementary steps. Because different processes (leading to different products) may include common elementary reactions, the UBI–QEP energetic estimates for these reactions are common and therefore form a database for multiple uses.

In this section we provide several examples of the recent UBI–QEP applications. Table 11 is a part of the UBI–QEP database which contains the intrinsic activation barriers of elementary reactions including various carbon-, oxygen-, and hydrogen-containing species and comprising the mechanisms of several interrelated processes such as the Fischer–Tropsch (FT) synthesis, methane conversion and hydrogen peroxide synthesis. Several more tables of the UBI–QEP data, particularly including reactions of nitrogen-containing species, will be added later. This tabulation is intended to give the reader a realistic sense of the scope and applicability of the UBI–QEP method. The amount of computational effort required to generate the UBI–QEP reaction energetics (enthalpies and activation barriers) is minuscule compared to the ab initio or DFT calculations.

In the examples below, we emphasize the chemical understanding that is obtained through applications of the UBI–QEP method beginning with a small number of thermodynamic observables. In these selected examples, reaction mechanisms are analyzed by considering the activation barriers for the individual elementary steps. Implicit in this process is the assumption that the reactions with the lowest activation barriers will dominate the mechanism. This is reasonable, since a difference of 5 kcal/mol in the activation barriers of two reactions translates into a difference in the reaction rates of a factor of 4160 at room temperature. If reactions have similar or zero intrinsic activation barriers, then one should consider the diffusion contributions to the apparent activation barriers.

As this section is devoted to the UBI–QEP analyses of surface reactions, we compare the UBI–QEP predictions only with the most relevant experimental data but not with other theoretical treatments of those reactions. Selective comparisons with other theoretical approaches are given in Section 10.

9.1. Fischer–Tropsch synthesis

In general, the Fischer–Tropsch (FT) synthesis refers to a general process of hydrogenation of CO by H$_2$ on catalytic metal surfaces, which produces a complex mixture of products consisting of methane,
Table 11
UBI-QEP reaction activation barriers, forward and reverse, for low coverage conditions on fcc(111) surfaces

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E^*_f$</th>
<th>$\Delta E^*_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Pd</td>
</tr>
<tr>
<td>CO $\rightarrow$ C + O</td>
<td>33</td>
<td>50</td>
</tr>
<tr>
<td>CH$_3$ + H $\rightarrow$ CH$_4$</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>CH$_2$ + H $\rightarrow$ CH$_3$</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>CH$_3$ + OH $\rightarrow$ CH$_3$OH</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td>CH$_3$ + OH $\rightarrow$ CH$_2$O + H</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>CH$_3$ + O$_2$ $\rightarrow$ CH$_3$O + O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$ + O $\rightarrow$ CH$_3$O</td>
<td>21</td>
<td>13</td>
</tr>
<tr>
<td>CH$_3$O + H $\rightarrow$ CH$_3$OH</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td>CH$_3$OH + H $\rightarrow$ CH$_3$OH</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>CH$_3$O + C $\rightarrow$ CO + CH$_3$</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$O $\rightarrow$ H$_2$CO + H</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$OH + O $\rightarrow$ CH$_2$OH + OH</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$OH + O$_2$ $\rightarrow$ CH$_2$OH + OOH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$OH + H $\rightarrow$ CH$_2$OH + H$_2$</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>CH$_3$OH + CH$_3$ $\rightarrow$ CH$_2$OH + CH$_4$</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>CH$_4$ + H $\rightarrow$ CH$_3$ + H$_2$</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>CH$_4$ + O $\rightarrow$ CH$_3$ + OH</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>CH$_4$ + O$_2$ $\rightarrow$ CH$_3$ + OOH</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>H$_2$CO $\rightarrow$ HCO + H</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>H$_2$CO + OOH $\rightarrow$ HCO + H$_2$O$_2$</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_6$</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>H$_2$O + H $\rightarrow$ OH</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>OH + OH $\rightarrow$ H$_2$O$_2$</td>
<td>81</td>
<td>55</td>
</tr>
<tr>
<td>OH + H$_2$ $\rightarrow$ H$_2$O + O</td>
<td>23</td>
<td>18</td>
</tr>
<tr>
<td>OOH + H $\rightarrow$ H$_2$O$_2$</td>
<td>29</td>
<td>18</td>
</tr>
<tr>
<td>OOH + H$_2$ $\rightarrow$ H$_2$O$_2$ + H</td>
<td>22</td>
<td>13</td>
</tr>
<tr>
<td>O$_2$ + O $\rightarrow$ O$_3$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*All energies are in kcal/mol. The calculated values are taken from Refs. [67–75].

olefins and paraffins, methanol and higher oxygenates (principally alcohols) [70,150]. For such a wide variety, there is no (and cannot be) universal catalyst, and the challenge is to find a proper catalyst to obtain selectively the desirable products. Clearly, hydrocarbons and higher oxygenates can be produced only after the CO dissociation (followed by carbon hydrogenation and carbon chain growth) but the formation of methanol requires the retaining of the C–O bond. These opposing requirements cannot be effectively fulfilled by the same catalyst, and indeed the known catalysts for the two processes are quite different. For this and historical reasons, the FT synthesis commonly refers only to the CO hydrogenation to higher hydrocarbons and oxygenates, but, the methanol synthesis from CO and H2 is treated separately. In this section we will discuss the UBI–QEP analyses of both the processes.

Despite enormous experimental efforts, many mechanistic aspects of the FT synthesis, particularly the periodic dependence of product selectivity, remain a subject of ongoing discussion [70,150–156]. The major questions are:
(1) Which metals might be the most efficient FT catalysts?
(2) What is the role of carburization of the catalytic metal surface?
(3) What is the preferred path for alkyl chain growth?
(4) What should be the primary FT hydrocarbon products?

The UBI–QEP method allows one not only to answer each of these (and other) questions but also to interrelate them within the unified energetic framework.

The UBI–QEP modeling of the FT synthesis of hydrocarbons has been made for the CO hydro-generation on densely packed surfaces of transition metals forming the periodic series of Cu(111), Pt(111), Ni(111), Fe(110) and W(110) [70]. Because the bcc(110) surfaces of Fe and W have very similar adsorption energetics, a model metal surface Fe/W(110) averaging those parameters was used. The analysis was based on comparisons of the calculated intrinsic activation barriers for 60 elementary reactions involving various C1 and C2 species on each of the four metal (Cu, Pt, Ni, Fe/W) surfaces. Comparing the activation barriers reveals which reactions are productive and which are inefficient.

The UBI–QEP calculations rely on the choice of the atomic binding energies. Direct experimental data on $Q_H$ and $Q_O$ exist for all the metals studied but $Q_C$ is known only for Ni, the values of $Q_C$ for other metals have been estimated [70]. To compensate for the uncertainties in $Q_C$, experimental values of $Q_{CO}$ were used. Since the only chemisorption data employed in the UBI–QEP analysis of the FT synthesis are the experimental values of $Q_A$ and $Q_{CO}$, all calculated numbers in Tables 11–13 and the projections based on these numbers are in fact predictions of the model.

The data in Ref. [70], Table 2 and Table 12 clearly demonstrate the periodic trends in the ability of metal surfaces to dissociate chemical bonds. Those to recombine the bonds are always opposite. Because the FT synthesis includes steps showing opposing trends, such as the dissociation of CO versus the recombination of the C–H (hydrogenation of C, CH, etc.) and C–C bonds (chain propagation) and product desorption, the optimal FT performance is a delicate balance of these competing influences. Specifically, from the data in Ref. [70] and in Tables 12 and 13, the major conclusions are:

(1) Direct dissociation of CO to form carbidic carbon may occur spontaneously on Fe/W and with a small activation barrier on Ni, but requires too high barriers on Pt and Cu. Hydrogen-assisted dissociation of CO is even more facile on Fe/W and Ni but more hindered on Pt and Cu.

(2) The preferred path for initiation of alkyl chain growth is the insertion of adsorbed CH$_2$ into the metal–carbon bond of an adsorbed CH$_3$ group. The barrier for this insertion decreases in the order Fe/W $>$ Ni $>$ Pt $\approx$ Cu (see Table 12).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cu</th>
<th>Pt</th>
<th>Ni</th>
<th>Fe/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ + CH$_2$</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>CH$_3$ + CH</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>CH$_3$ + C</td>
<td>7</td>
<td>10</td>
<td>29</td>
<td>43</td>
</tr>
<tr>
<td>CH$_2$ + CH$_2$</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>34</td>
</tr>
<tr>
<td>CH$_2$ + CH</td>
<td>0</td>
<td>2</td>
<td>18</td>
<td>39</td>
</tr>
</tbody>
</table>

*The zero intrinsic barrier indicates that the reaction is diffusion-controlled (see Section 4.7).*
The table below shows the dissociation of CO on Fe(1 0 0): coadsorption effects on Q and ΔE*.

<table>
<thead>
<tr>
<th>Surface</th>
<th>θ_{CO}</th>
<th>Q_c</th>
<th>Q_o</th>
<th>Q_{CO}</th>
<th>ΔE_{CO,Δ}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1 0 0)</td>
<td>0</td>
<td>200</td>
<td>120</td>
<td>34</td>
<td>-11</td>
</tr>
<tr>
<td>Fe(1 0 0)-c(2 × 2)C, O</td>
<td>0.5</td>
<td>178</td>
<td>82</td>
<td>20</td>
<td>16</td>
</tr>
</tbody>
</table>

- All values in kcal/mol.
- Experimental estimates taken from Ref. [39].
- UBI-QEP calculated values.
- Calculated using Eq. (4.6.3.3) (or explicitly from Eq. (7) of [70]) for D_{AB} = 257 kcal/mol.

(3) Metallic Fe is necessary to produce the abundance of carbidic carbon from CO but the synthesis of hydrocarbons and oxygenates can effectively proceed only on carbided Fe surfaces which resemble the less active metals such as Pt (cf. Tables 11 and 13). Transformation of the carbidic carbon into a product, which eventually desorbs, restores the Fe catalyst’s ability to dissociate CO and starts a new FT cycle.

(4) On Fe/W, Ni, and, Pt, the smaller barriers for β-hydrogen elimination than for α-hydrogen addition indicate that olefins rather than paraffins will be the primary FT hydrocarbon products.

These and other UBI-QEP model projections [70] are fully consistent with diverse experimental studies which were discussed in detail in [70] and will not be repeated here. Instead we concentrate on model predictions that had been tested after their publication [70] in recent mechanistic studies involving formation of alkyl species by thermal [151] or photochemical [152] dissociation of alkyl halides on metal surfaces.

First, the UBI-QEP analysis predicted that methylene, CH₂, is the active chain growth species, and the barrier for the methylene insertion into the metal–CH₃ bond decreases in the order Fe > Ni > Pt > Cu, so the insertion should be most facile on Cu surfaces. The resulting ethyl and higher alkyls (formed by successive CH₂ insertion) were predicted to undergo β-hydrogen elimination to form olefins. All this has been directly confirmed by Bent and co-workers [153] who found that radicals CH₃ and CH₂ (obtained by thermal decomposition of CH₃I and CH₂I₂, respectively) easily recombined into ethyl to form ethylene on Cu(1 0 0) and into propyl, C₃H₇, to form propylene on Cu(1 1 0).

Second, because the UBI-QEP recombination activation barriers decrease with a decrease of energies of the metal–adsorbate bonds involved, all recombination reactions, including hydrogenation and C–C chain growth, were predicted to be more facile on surfaces of IB group metals Cu, Ag, and Au than on those of transition metals. Accordingly, Paul and Bent [154] have found that methyl coupling was very facile on Cu(1 1 1), Ag(1 1 1) and Au(1 0 0) surfaces, the coupling rate being faster on a surface with the weaker metal–carbon bond. The recent experimental data on the periodic regularities in stability and reactions of CH₂ and CH₃ species on surfaces of Ag, Cu, Pd, Pt and Rh [151–155] further corroborated the predicted UBI-QEP patterns.

Recent studies employing doubly labeled ¹³C₂ probes, ethylene, ¹³C₂H₄, and vinyl bromide, ¹³C₂H₃Br [154], suggested that the C–C-chain growth may occur via the methylene insertion into vinyl, CH=CH₂, to form eventually propenyl CH=CH–CH₃, which further combines with more methylene to form higher alkenyls. The cycle is terminated by hydrogenation of the alkenyl, giving the alkene.
Since the alkenyl mechanism involves polyatomic species that are too large to be accurately treated by any theoretical method, this alternative mechanism, which leads to the same olefin products, cannot be theoretically analyzed at this time.

9.2. Oxygen-assisted X–H bond cleavage

The cleavage of X–H bonds, where X = O, N, C, is an important starting point in many catalytic reactions [149] including the direct conversion of methane to methanol described in Section 9.4.2. For processes occurring on Ag and Au, which do not directly dissociate these bonds, the X–H bond activation should be assisted. Within the UBI–QEP framework, in order to decrease the activation barrier for the X–H bond dissociation, an assisting coadsorbate should make the reaction (much) more exothermic. The natural choice for the coadsorbate is atomic oxygen which forms strong O–H bonds. The UBI–QEP analysis [149] included 18 reactions involving the cleavage of X–H bonds with and without the involvement of atomic oxygen on Cu(111), Ni(111), W(110) and Ag(111). The dissociating species were CH₄, CH₃OH, HCOOH and NH₃, which produce hydroxyl in the presence of oxygen. Since hydroxyl may form hydrogen bonded islands [130], the OH heat of adsorption used in the UBI–QEP calculations may or may not include the additional stabilization from the hydrogen bonds. Below, we quote results that both include and ignore this stabilization. The X–H bond dissociations, direct and involving adsorbed atomic oxygen can be represented as

\[
\text{direct:} \quad H-X(ad) \rightarrow H(ad) + X(ad), \tag{9.2.1}
\]
\[
\text{oxygen-assisted:} \quad H-X(ad) + O(ad) \rightarrow X(ad) + OH(ad) \tag{9.2.2}
\]
or
\[
H-X(ad) + O(ad) \rightarrow Y(ad) + H_2O(ad), \tag{9.2.3}
\]
where Y is a compound that has one less hydrogen than X. In both these reactions the oxygen bearing product is a quite stable molecule. Comparing the activation barriers with and without the participation of oxygen shows the influence on the reaction rates of oxygen participation.

Based on comparisons of the calculated heats of adsorption, \(Q\), and activation barriers, \(\Delta E^*\), the primary result of the UBI–QEP analysis is that the presence of low coverages of coadsorbed oxygen basically reverses the sequence of activities of the metals for H–X bond cleavage. As can be seen from Table 14, in the absence of oxygen, the activity series for H–X bond cleavage is W > Ni > Cu > Ag, where Ag cannot dissociate H–X bonds. By contrast, a low coverage of oxygen inhibited the H–X bond dissociation on W and Ni but facilitated it on Cu and Ag making the W surface the least active, but, the Ag surface the most active. This effect is even more pronounced when the island forming tendency of OH is taken into account [130,149,157]. In particular, when OH islands are formed on Ag(111), the CH₃O–H dissociation barrier of 11 kcal/mol becomes comparable with the CH₃OH desorption barrier, \(Q_{CH₃OH} \approx 10\) kcal/mol [149], so the Ag surface is projected to dissociate the CH₃O–H bond, in agreement with experiment [149,157]. This analysis corroborated, quantitatively and for the first time, the energetic origin of the oxygen-assisted bond cleavage which plays so important a role in heterogeneous catalysis [149].
Table 14
Activation barriers, $\Delta E_{X-H}^c$ (kcal/mol), for the X-H dissociation on W(110), Ni(111), Cu(111) and Ag(111)

<table>
<thead>
<tr>
<th>X-H</th>
<th>Unassisted $^a$</th>
<th>Oxygen-assisted $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>Ni</td>
</tr>
<tr>
<td>CH$_3$-H$^c$</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>NH$_2$-H$^c$</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>CH$_3$O-H$^c$</td>
<td>10</td>
<td>13</td>
</tr>
</tbody>
</table>

$^a$Eq. (9.2.1).
$^b$Eq. (9.2.2).
$^c$Results do not account for inter-adsorbate hydrogen bonding [149].
$^d$Results account for inter-adsorbate hydrogen bonding [130].

9.3. Hydrogen peroxide synthesis

Hydrogen peroxide is an important industrial chemical due to its efficacy as an environmentally benign bleaching agent. The hydrogen peroxide synthesis considered starts with H$_2$ and O$_2$ as reactants and involves 40 elementary reactions each on fcc(111) surfaces of Pd, Pt, Ag and Au [68]. One may consider the mechanism to be composed of two major reaction channels; one involving the OOH intermediate and the other involving the hydroxyl intermediate. The path between the two main channels is a one-way-path through which surface H$_2$O$_2$ decomposes to hydroxyls. The mechanism can be represented schematically in an over-simplified way as:

$$\text{OOH} \rightarrow\rightarrow H_2O_2$$

$$H_2 + O_2 \rightarrow\rightarrow H_2O_2$$

$$\rightarrow\rightarrow OH \rightarrow\rightarrow H_2O$$

The enthalpies and activation barriers were computed at high and low coverages, and the optimum conditions for H$_2$O$_2$ synthesis were deduced from these UBI-QEP data [68]. Tables 15 and 16 contain activation barriers for selected reactions for coverages of atomic oxygen of $\theta = 0$ and 0.6, respectively. Emphasis has been placed on reactions of formation and decomposition of the crucial OOH intermediate.

The major modeling conclusions are:

(1) The synthesis of H$_2$O$_2$ takes place via the OOH intermediate and not through the reaction of two hydroxyls. Reactions forming hydroxyl should be inhibited and lead primarily to the formation of water.

(2) High oxygen coverages favor the OOH mechanistic path as do other promoters. At higher coverages, the stability of hydroxyl is reduced thereby favorably increasing the decomposition
Table 15
UBI-QEP intrinsic activation barriers, $\Delta E^*$ (kcal/mol), for selected reactions involved in the hydrogen peroxide synthesis on fcc(1 1 1) surfaces, for the zero coverage limit

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 \rightarrow 2\text{H}$</td>
<td></td>
<td>9</td>
<td>9</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>$\text{O}_2 \rightarrow 2\text{O}$</td>
<td></td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \rightarrow \text{OOH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{OOH} \rightarrow \text{O}_2 + \text{H}$</td>
<td></td>
<td>17</td>
<td>17</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>$\text{OOH} \rightarrow \text{OH} + \text{O}$</td>
<td></td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>$\text{OOH} + \text{H} \rightarrow \text{H}_2\text{O}_2$</td>
<td></td>
<td>18</td>
<td>17</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>$2\text{OH} \rightarrow \text{H}_2\text{O}_2$</td>
<td></td>
<td>42</td>
<td>43</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>$\text{OOH} + \text{H} \rightarrow 2\text{OH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2(\text{gas})$</td>
<td></td>
<td>14</td>
<td>14</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$</td>
<td></td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$\text{O} + \text{OH} \rightarrow \text{OOH}$</td>
<td></td>
<td>34</td>
<td>34</td>
<td>30</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 16
UBI-QEP intrinsic activation barriers, $\Delta E^*$ (kcal/mol), for the reactions in Table 15 at an atomic oxygen coverage $\theta = 0.6$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 \rightarrow 2\text{H}$</td>
<td></td>
<td>9</td>
<td>9</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>$\text{O}_2 \rightarrow 2\text{O}$</td>
<td></td>
<td>17</td>
<td>18</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \rightarrow \text{OOH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$</td>
<td></td>
<td>8</td>
<td>9</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>$\text{OOH} \rightarrow \text{O}_2 + \text{H}$</td>
<td></td>
<td>10</td>
<td>10</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>$\text{OOH} \rightarrow \text{OH} + \text{O}$</td>
<td></td>
<td>14</td>
<td>15</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>$\text{OOH} + \text{H} \rightarrow \text{H}_2\text{O}_2$</td>
<td></td>
<td>10</td>
<td>9</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$2\text{OH} \rightarrow \text{H}_2\text{O}_2$</td>
<td></td>
<td>21</td>
<td>20</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>$\text{OOH} + \text{H} \rightarrow 2\text{OH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2(\text{gas})$</td>
<td></td>
<td>10</td>
<td>10</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$\text{O} + \text{OH} \rightarrow \text{OOH}$</td>
<td></td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

The modeling suggests that the most efficient way to accomplish the desired suppression of hydroxyl formation is through the use of a non-reactive additive that will effectively block active sites of $\text{H}_2\text{O}_2$ dissociation. Halide promoters, such as $\text{Br}^-$ and $\text{Cl}^-$, might have desirable properties [68].

(3) Hydrogen peroxide cannot be produced from reactions of $\text{H}_2$ and $\text{O}_2$ on noble metal surfaces at low coverage. Under these conditions, any hydrogen peroxide that is formed decomposes quickly to hydroxyl. The formation of the important OOH intermediate will be more successful on gold, however, gold is still able to decompose hydrogen peroxide at low coverages.
The patent literature [158–167] contains essentially all the published experimental data on hydrogen peroxide synthesis on metal surfaces. Since these data are usually confined to descriptions of experimental conditions and yields, a detailed comparison of our UBI-QEP results with experimental ones is not presently possible. We point out, however, that the optimum conditions predicted on the basis of UBI-QEP modeling are consistent with those described in the patent literature [158–167] for successful H₂O₂ synthesis strategies. In all cases high O₂ to H₂ pressure ratios were employed, which cause a high surface coverage of O₂ and atomic oxygen, the latter of which can act as a self-promoter. In addition, most cases employ a halide promoter which the UBI-QEP modeling indicates should play an important role. The modeling recommendation that Au should be an adequate unimetal catalyst for hydrogen peroxide synthesis is supported by the recent patent by Lueckoff et al. [167] for the synthesis of hydrogen peroxide over gold. This patent indicates that the synthesis method produces hydrogen peroxide at high rates and high selectivity.

9.4. Methanol synthesis

UBI-QEP analyses of the two main methanol processes, the direct conversion of methane to methanol [67] and the synthesis of methanol via the hydrogenation of CO and CO₂ [69], have been performed. There is some overlap between the Fischer–Tropsch synthesis and the methanol synthesis. The mechanisms considered in the analyses are composed of a total of more than 450 elementary reaction steps each taking place on close-packed surfaces of Cu, Ni, Pd, Pt and Au. The scope of the methanol work is too large to be reproduced here in detail, so we summarize just the more important questions and illustrate how they were addressed within the framework of the UBI-QEP method.

9.4.1. Hydrogenation of CO and CO₂

The analysis [69] compared the formyl, HCO, and formate, HCOO, routes to methanol starting from CO and CO₂ on the fcc(1 1 1) surfaces of Cu and Pd, the metals known as effective catalysts for the methanol synthesis:

\[ \text{CO(ad)} + \text{H-source} \Rightarrow \text{HCO(ad)} \Rightarrow \text{CH₃OH(ad)} \]  \hspace{1cm} (9.4.1.1)

\[ \text{CO}_2\text{(ad)} + \text{H-source} \Rightarrow \begin{cases} \text{HCOO(ad)} \Rightarrow \text{CH₃OH(ad)} \\ \text{water + CO + H-source} \Rightarrow \text{CH₃OH(ad)} \end{cases} \]  \hspace{1cm} (9.4.1.2)

The analysis also had the goal of understanding the role of the reverse water-gas-shift (WGS) reaction, which may be a competitive route during the hydrogenation of CO₂. The activation barriers for the reactions involved on each metal were computed and compared with each other as well as with the desorption barriers of the reactants. This gives insight into which reactions should dominate the mechanism based on the rule of thumb that the reactions with the lowest barriers are the most important. Selected activation barriers are given in Table 17.

The primary modeling conclusions are:

(1) The formyl route to methanol (Eq. (9.4.1.1)) is effective on Pd but not on Cu. On Cu the barrier to desorption of CO is less than the barrier to formation of formyl, so, CO should desorb before it hydrogenates. On Pd, the two barriers are similar, so that formyl formation should take place.
Table 17
Intrinsic activation barriers, $\Delta E^*$ (kcal/mol), for various surface processes in the hydrogenation of CO and CO$_2$ over Pd(1 1 1) and Cu(1 1 1)$^a$

<table>
<thead>
<tr>
<th>Process</th>
<th>Cu</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO desorption</td>
<td>12</td>
<td>34</td>
</tr>
<tr>
<td>CO + H $\rightarrow$ HCO</td>
<td>24</td>
<td>35</td>
</tr>
<tr>
<td>CO + OH $\rightarrow$ HCOO</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>CO + OH $\rightarrow$ CO$_2$ + H</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>CO + OH $\rightarrow$ HCO + O</td>
<td>39</td>
<td>27</td>
</tr>
<tr>
<td>HCOO + H $\rightarrow$ H$_2$CO + O</td>
<td>19</td>
<td>32</td>
</tr>
<tr>
<td>HCOO $\rightarrow$ CO$_2$ + H</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$ desorption</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>CO$_2$ + H $\rightarrow$ HCOO</td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$Results do not account for inter-adsorbate hydrogen bonding [69].

(2) The formate path to methanol (Eq. (9.4.1.2)) is efficient on Cu, but not on Pd. On Pd the reactant, CO$_2$, desorbs before reaction. On Cu, the desorption and hydrogenation barriers of CO$_2$ are 5 and 4 kcal/mol, respectively, so the formate formation is competitive with CO$_2$ desorption.

(3) The rate determining step in the formate path on Cu is the hydrogenolysis of formate to surface formaldehyde and atomic oxygen. Although the modeling projects that formate should readily form on Cu via the reaction between CO and OH as well as CO$_2$ and H, formate should also readily decompose to CO$_2$ + H.

(4) The dissociation of water is projected to be the rate determining step in the water-gas-shift reaction, and the reverse of the water-gas-shift reaction is projected to be competitive with methanol formation over Cu.

These and other model projections are in good agreement with experimental data [69].

9.4.2. Direct conversion of methane to methanol

In the direct conversion of methane to methanol, one seeks the shortest possible route (the one with the fewest number of steps) between surface methane and methanol. Given this, one seeks to avoid too much hydrogen extraction from methane as well as over-oxygenation of carbonaceous compounds. It is also critical that the metal surface does not catalyze the decomposition of the desired product. The mechanism considered [67] is composed of 400 elementary reactions each on four different fcc(1 1 1) metal surfaces. The reaction enthalpies and activation barriers for these 400+ reactions on close-packed surfaces of Ni, Pd, Pt and Au were computed and compared to determine the optimum conditions for methanol synthesis.

As is usually the case, desirable periodic trends often go in opposite directions in a metal series, so the optimization of a process amounts to achieving a balance among competing influences. The UBI–QEP analysis suggests a set of conditions that are more favorable for the formation of methanol from methane and oxygen, and suggests that the least active of the noble metals, such as gold, would be more suitable than more active metals.

The most important role of oxygen is to get the process started by abstracting a hydrogen from CH$_4$. In Section 9.2 we discussed the ability of oxygen to assist the cleavage of C–H bonds on the lesser
Table 18

Intrinsic activation barriers, $\Delta E^*$ (kcal/mol), for some reactions involved in the direct conversion of methane to methanol on fcc(1 1 1) metal surfaces$^a$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O $\rightarrow$ H$_2$CO</td>
<td>9.5</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>CH$_3$O + O $\rightarrow$ H$_2$CO + OH</td>
<td>22</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H$_2$CO + O $\rightarrow$ HCO + OH</td>
<td>11</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CH$_3$ + OH $\rightarrow$ CH$_3$OH</td>
<td>22</td>
<td>12</td>
<td>9</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>CH$_3$O + H $\rightarrow$ CH$_3$OH</td>
<td>19</td>
<td>8</td>
<td>6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH + O $\rightarrow$ CH$_3$OH + OH</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH + O$_2$ $\rightarrow$ CH$_3$OH + OOH</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH + OH $\rightarrow$ CH$_2$OH + H$_2$O</td>
<td>10</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Results account for inter-adsorbate hydrogen bonding between surface hydroxyls [67].

active noble metals. However, the oxygen surface species must be kept at a relatively low concentration because, as the data in Table 18 show, they also stimulate the decomposition of methoxy, methanol and formaldehyde [67], which are steps in the wrong direction. Therefore, one should create conditions under which the oxygen is, as completely as possible, consumed in the hydrogen abstraction from methane. One way to achieve this is to preload the catalyst with methane and keep the ratio of methane-to-oxygen high. In this mechanism, the most successful paths for methanol synthesis are the reactions between methyl and hydroxyl radicals and the hydrogenation of methoxy. On gold methane serves as both the hydrogen source as well as the methyl source. This is an important point, since the hydrogen source might account for a significant part of the expense of this process.

The main conclusion from the modeling is that the direct conversion of methane to methanol should be possible on gold. Also, UBI-QEP analysis shows that the synthesis of some amount of formaldehyde is unavoidable with oxygen as the oxygen source. The presence of formaldehyde may or may not be a problem, depending on the application. For example, contamination by formaldehyde might be tolerated in motor fuels. However, with hydrogen peroxide as the oxygen source, the model projections are [67] that formaldehyde synthesis will be limited in favor of methanol, particularly on gold.

9.5. Decomposition and reduction of NO

Nitrogen oxides, particularly NO, are major noxious pollutants produced from automotive and various stationary sources [168]. The use of catalytic converters containing transition metals such as Pt, Rh and Pd for the abatement of NO has resulted in rapidly growing efforts in academia and industry to understand the catalytic chemistry of NO on surfaces of these metals. The central issues here are the possible pathways by which NO can be decomposed, preferably directly, into atomic N and O, or alternatively, reduced by other coadsorbates, particularly by CO or H$_2$ to form and eventually desorb N$_2$ and CO$_2$, or NH$_3$ and H$_2$O [169]. Experimental studies have revealed significant differences in catalytic activity and selectivity as a function of metal composition. Although various separate aspects of the NO chemistry have been treated theoretically, until recently, a coherent theoretical framework for explaining the diverse experimental observations was lacking.
Table 19
Calculated UBI–QEP values of Q: comparison with experiment

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Q (kcal/mol)</th>
<th>calc.</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>Pt(111)</td>
<td>11–14</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ru(001)</td>
<td>16–18</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Re(001)</td>
<td>20</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>NH₂</td>
<td>Pt(111)</td>
<td>39–47</td>
<td>&gt;42</td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>Pt(111)</td>
<td>71</td>
<td>71–74</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>Pt(111)</td>
<td>28ᵇ</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rh(111)</td>
<td>28ᵇ</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ru(001)</td>
<td>31–34</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Pt(111)</td>
<td>11</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

ᵃAll data from Table 3 in Ref. [72] with corrections for NO for Pt(111) and Rh(111).
ᵇCalculated for the hollow site, as determined by the latest experiments [229].
ᶜThe latest measurement [170].

The UBI–QEP method has provided such a framework by analyzing periodic trends in the decomposition of NO and its reduction to N₂ and NH₃ by CO and H₂ on transition metal surfaces [72]. As the periodic series, the close-packed surfaces Pt(111), Rh(111), Ru(001) and Re(001) were chosen. Regarding the atomic binding energies of N and O, the direct experimental data exist for Q_N only on Re and for Q_O on Pt and Rh; the other energies have been estimated. The calculated heats of molecular chemisorption were in good agreement with experiment, as illustrated in Table 19.

With these values of Q, the reaction enthalpies and intrinsic activation barriers were calculated for 48 appropriate elementary reactions for each of the four metal (Pt, Rh, Ru, Re) surfaces [72]. Some selected data are shown in Table 20.

The major model projections are the following:

1. For Pt(1 1 1) and Rh(1 1 1), the values of Q_N are very close but those of Q_O strongly differ. The much larger value of Q_O for Rh is the primary reason for the higher ability of Rh to dissociate NO.
2. The NO dissociation is highly exothermic on all metal surfaces studied with the exothermicity increasing in the order Pt < Rh < Ru < Re. The intrinsic activation barriers for the NO dissociation (∆E_{NO,s}⁻) decrease in this order vanishing on Ru and Re. In the zero coverage limit, these barriers are much smaller than the appropriate desorption barriers of NO (Q_{NO}), so all the surfaces are projected to thermally dissociate NO (with the possible exception of Pt(1 1 1), where the difference between Q_{NO} and ∆E_{NO,s}⁻ may be small enough to make dissociation and desorption of NO competitive).
3. The presence of adsorbed N and O atoms may dramatically increase the values of ∆E_{NO,s}⁻ (the situation is analogous to the effect of carbidic carbon in the FT synthesis on Fe surfaces, discussed above). The high sensitivity of the values of ∆E_{NO,s}⁻ to adsorbate coverage may affect the experimental outcome for different NO exposures.
4. The intrinsic N–N recombination barriers rapidly increase in the order Pt ≈ Rh ≪ Ru ≪ Re, so the Pt and Rh surfaces are most efficient for the formation of N₂. The presence of atomic hydrogen
Table 20
UBI-QEP energetics for low coverage desorption and decomposition of NO and its reduction by CO and H₂ on Pt(1 1 1), Rh(1 1 1), Ru(00 1) and Re(00 1)

<table>
<thead>
<tr>
<th>Surface reaction</th>
<th>Pt</th>
<th>Rh</th>
<th>Ru</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH</td>
<td>ΔE*</td>
<td>ΔH</td>
<td>ΔE*</td>
</tr>
<tr>
<td>NO → N + O a</td>
<td>-24</td>
<td>13</td>
<td>-41</td>
<td>7</td>
</tr>
<tr>
<td>N + O → NO(g)</td>
<td>-16</td>
<td>15</td>
<td>-33</td>
<td>9</td>
</tr>
<tr>
<td>NO + N → N₂(g) + O</td>
<td>-18</td>
<td>&lt;21</td>
<td>-39</td>
<td>&lt;21</td>
</tr>
<tr>
<td>N + N → N₂(g)</td>
<td>6</td>
<td>27</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td>NO + CO → N + CO₂</td>
<td>-38</td>
<td>39</td>
<td>-50</td>
<td>53</td>
</tr>
</tbody>
</table>

a Two sets of values are given obtained from the upper and lower limits of the estimates for the atomic heats of adsorption of N and O [72]. Note that the values of ΔE* are close despite possible large differences in ΔH.
b All species are adsorbed unless otherwise indicated.

decreases the NO dissociation barrier on both Pt and Rh. As a result, Rh and/or Rh–Pt surfaces appear to be the most efficient catalysts for NO reduction by CO to form N₂ and CO₂, but Pt surfaces appear to be more efficient for NO reduction by H₂ to form NH₃ and H₂O.

These and other UBI–QEP predictions are in agreement with diverse experimental data discussed in detail in Ref. [72].

From later corroborations of the UBI–QEP calculations of the NO energetics, we mention here only the comprehensive work by Borg et al. [170]. By using temperature programmed static secondary ion mass spectrometry (TPSSIMS) and temperature programmed desorption (TPD) methods, they studied the kinetics of the dissociation and desorption of NO and the desorption of N₂ on Rh(1 1 1) for various coverages. The dissociation rate, modeled by an Arrhenius-type differential equation, was assumed to be proportional to the nth power of the (normalized) absolute coverage of available sites. The parameter n can be considered as an effective ensemble size required for dissociation of NO to N and O. This differential equation was integrated numerically for independent values of the pre-exponential factor, ν, and activation energy, ΔE*, to obtain the best fit for both the measured NO~ and N~ concentrations. It was found [170] that for a given dissociation rate, the experimental values of ΔE* may vary, depending on n leading to compensating changes in ν (compensation effect). Specifically, for n = 0–4, the values of ΔE* and ν increase within the range 9–17 kcal/mol and 10⁶–10¹² s⁻¹, respectively [170]. The case of n = 0 assumes pure first-order dissociation kinetics with no site blocking which fits well the experimental dissociative picture at very low coverages of 0.15–0.20 ML, so we choose the proper value of ΔE* = 9 kcal/mol for comparison. Other experimental values, of the intrinsic activation barriers for the NO desorption, QNO, and N–N recombination, ΔE*ₐₐₙ, were taken also for the zero coverage limit. The experimental data are collected in Table 21, where they are compared with the appropriate UBI–QEP values [72] in excellent agreement.

The above quantitative estimates of Q and ΔE* have been obtained for low coverages. At higher coverages, the energetics may be affected significantly. For example, for a Rh(1 0 0)–c(2 × 2) O,N surface, which corresponds to a total adatom coverage of 0.5 ML (θN = θO = 0.25) , the UBI–QEP values are QNO = 18 kcal/mol and ΔE*ₐₐₙ = 27 kcal/mol [72]. In other words, partially nitrided
(oxidized) Rh surfaces may not be efficient in dissociation of NO until the appropriate excess of adsorbed N and O is removed from the surface by desorption or surface reaction (cf. the similar conclusion in Section 9.1 regarding the role of carbided Fe surfaces in the FT synthesis). Experimental data on various metal surfaces [169] support the UBI-QEP predictions of strong coverage dependence of the NO reactivity.

In summary, the UBI-QEP method provides rather accurate estimates of molecular heats of adsorption, \( Q \), and activation barriers, \( \Delta E^* \), for a wide variety of elementary reactions relevant to the NO chemistry on catalytic metal surfaces. Given that all the calculated values of \( Q \) and \( \Delta E^* \) are internal model predictions, and when the appropriate experimental values are available, they are consistent with experiment, the validity of the UBI-QEP method for quantitative energetic estimates is manifest.

The projected qualitative patterns of the NO reactivity, based on values of the relevant UBI-QEP activation barriers, are broadly consistent with experiment as well, although some of the features appear to be more complex. One should recall that the activation barrier may be a good measure of reactivity only if the pre-exponential factors of the compared reactions are close enough, which in principle should be verified by independent determinations of \( \nu \). In practice, however, the values of \( \nu \) are usually assumed, most commonly as \( \nu = 10^{13} \text{ s}^{-1} \) for first-order reactions. In particular, for the NO dissociation on Rh(1 1 1), the estimated range of \( \nu = 10^{12} - 10^6 \text{ s}^{-1} \) [179] appears to be much smaller. For the NO dissociation on Rh(1 1 0), the pre-exponential factor further reduced to about \( 10^2 \text{ s}^{-1} \) [171]. For this reason the dissociation rates of NO on Rh(1 1 1) and Rh(1 1 0) were found to be comparable [170,171] even though the NO dissociation barrier on Rh(1 1 0) was estimated to be only 4–5 kcal/mol, compared to 9 kcal/mol on Rh(1 1 1).

In such cases when the pre-exponential factors significantly differ, the UBI-QEP projections of reactivity based entirely on the values of \( \Delta E^* \) may be inconclusive and even inconsistent. Later we will encounter a similar situation in the case of the \( \text{N}_2 \) dissociation.

9.6. Ammonia synthesis

The mechanisms of ammonia decomposition, and synthesis from \( \text{N}_2 \) and \( \text{H}_2 \) on densely packed surfaces of Pt, Ru, Fe and Re have been analyzed using the UBI-QEP method [71]. The heats of adsorption for \( \text{NH}_y \) (\( y = 1, 2, 3 \)) species and the activation barriers for more than 70 elementary reactions thought to be important in the mechanisms were computed. Several issues were addressed:

(a) periodic regularities of dissociation and recombination reactions;
The calculated heats of molecular adsorption are shown in Table 22, where they are compared with relevant experimental data. The agreement is close indeed.

The barriers for selected reactions are given in Table 23 and compared with available experimental values. From these data, the primary conclusions are:

1. The activation barriers for bond dissociation decrease along the periodic series Pt > Ru > Fe > Re.
2. The activation barrier for the dissociative adsorption of N₂ increases sharply in the series Re ≤ Fe ≤ Ru ≪ Pt so that the ammonia synthesis is not possible on Pt.
3. The recombination and desorption barriers increase along the periodic series Pt < Ru < Fe < Re.
4. On all surfaces the largest activation barrier corresponds to the recombinative desorption of N₂.

This is the rate determining step in ammonia decomposition for which Pt, having the smallest barrier, is the most efficient catalytic metal.
These and other conclusions are in agreement with diverse experimental data discussed in detail in [71], and therefore, are not repeated here. We mention only some seemingly inconsistent results. Various experimental mechanistic studies of the ammonia synthesis on Fe, Ru and Re surfaces have demonstrated that the dissociative adsorption of N\textsubscript{2} is the rate limiting step [172,173]. In apparent contradiction, the UBI–QEP activation barriers for the N\textsubscript{2} dissociation on Fe and Re are much smaller than the barriers for the subsequent N–H recombination and even NH\textsubscript{3} desorption.

However, the calculated UBI–QEP values of $\Delta E^*$ for the N\textsubscript{2} dissociation are accurate, being 5 kcal/mol for Fe(1 1 0) and 4 kcal/mol for Re(00 1) compared to the experimental values of 7 [174] and 3 [175] kcal/mol, respectively. Clearly, this is not a failure of the UBI–QEP method. The relative slowness of the N\textsubscript{2} dissociation must be attributed to factors other than the activation barrier. Indeed, it has been found that the sticking coefficients for dissociative adsorption of N\textsubscript{2} on Fe(1 1 0) and Re(00 1) have exceptionally low values in the range $10^{-5}$–$10^{-6}$ [172,174,175].

Another seemingly inconsistent UBI–QEP result is the high activation barrier for the first hydrogenation of atomic N which was calculated to be within the range 36–42 kcal/mol (Table 23). This barrier appears to be too high for the reaction to occur. However, the barrier rapidly decreases with atomic nitrogen coverage. For example, for N coverage between 0.25 and 0.5 ML on the resulting bcc Fe(1 0 0)–c(2 × 2)N surface, the UBI–QEP value of $Q_N$ is lower than its zero coverage value by almost 30 kcal/mol, giving a value close to that for Pt(1 1 1) [71]. Thus, the UBI–QEP analysis predicts, preceeding experimental verification, that the ammonia synthesis occurs not on clean but nitrided surfaces of Fe and Re [71]. The conclusion is similar to that in the Fischer–Tropsch synthesis, where the hydrogenation of carbon species was predicted to occur not on clean but carbided Fe surfaces, in agreement with experiment (Section 9.1).

Finally, we cite an example of an experimental work to which the UBI–QEP results were inappropriately referred. The case is a recent kinetic study by Hardeveld et al. [176] of the mechanism of NH\textsubscript{3} formation by the hydrogenation of atomic N on Rh(1 1 1). The authors compared their findings for Rh(1 1 1) with the low coverage UBI–QEP analysis on Pt(1 1 1) [71] and claimed seeming discrepancies namely:

(1) the rate-determining step is the hydrogenation of NH\textsubscript{2} rather than N;
(2) desorption of NH\textsubscript{3} is preferred over dissociation.

As far as the rate-determining step is concerned, we believe that without knowledge of pre-exponential factors and activation barriers of assumed elementary steps, the pure kinetic analysis [176] is not unequivocal. This leaves only the issue of desorption versus dissociation of NH\textsubscript{3}, which in the UBI–QEP method is the matter of relative values of the relevant activation barriers. In other words, one can use the UBI–QEP data for Pt(1 1 1) to interpret the picture on Rh(1 1 1) only if the relative order of the barriers is the same. But it appears that this is not the case. Although for both Pt(1 1 1) and Rh(1 1 1) the experimental values of the atomic binding energy, $Q_N$, are not known, the latter for Rh appears to be larger. It may be calculated (using Eq. (4.2.1.4)) from the experimental value of $Q$ for NH\textsubscript{3}. This value, assuming a pre-exponential factor of $10^{13}$, was estimated (by the same authors) to be around 20 kcal/mol [177], which corresponds to $Q_N = 140$ kcal/mol. This value is much higher than for Pt (~116 kcal/mol) and comparable to that for Fe and Re (cf. Table 22). However for Fe and Re, under low coverages, the UBI–QEP analysis predicts the NH\textsubscript{3} dissociation to be preferred over desorption, opposite to the pattern for Pt, which is in agreement with the findings of Hardeveld et al. [176]. Moreover, for the activation barrier for the hydrogenation of NH\textsubscript{2} to NH\textsubscript{3}(g) on Rh(1 1 1),
the experimental estimate of 18 kcal/mol [176] is within the UBI-QEP range 17–20 kcal/mol (see Table 23).

9.7. Sulfur oxide chemistry

The sulfur oxide study [74] addressed a mechanistic understanding of the diverse SO₃ chemistry on fcc(1 1 1) surfaces of Ni, Cu, Ag, Au, Pd, and Pt. The major experimental results [178–195] to be explained by the modeling can be summarized as [74]: (a) no SO₂ has been observed to dissociate on Ag, (b) SO₂ is observed to dissociate on Ni surfaces at elevated temperatures and to a small extent on Cu, Pd and Pt, (c) the only sulfur oxide species observed to desorb from Cu and Ni group metals at low coverages is SO₂, and (d) contradictory interpretations of experimental data concerning the nature of SO, SO₂, SO₃ and SO₄ adsorbed species have been reported.

First, high quality ab initio calculations were performed on several metal surfaces in order to determine trends in the preferred coordination modes and binding sites of sulfur oxides [75]. These ab initio adsorbate geometries were used in the UBI–QEP calculations of molecular heats of adsorption, reaction enthalpies and activation barriers.

Table 24 offers a comparison of the desorption and dissociation barriers for sulfur oxides on the Cu and Ni group metals. Two decomposition paths for SO₂ were considered: (1) an asymmetric path: SO₂ → SO + O, and (2) a symmetric path: SO₂ → S + O + O. These paths are distinguished in Table 24 by subscripts ‘a’ and ‘s’, respectively. The barriers to the asymmetric SO₂ decomposition to SO and O are prohibitively high on all the Cu and Ni group metals. However, the symmetric dissociation, analogous to the symmetric stretching vibration of SO₂, to S + O + O is favored on Ni, and the dissociation barrier on Cu is competitive with the desorption barrier. This new mode of dissociation for SO₂ has not been discussed before in the literature. The modeling indicates that no direct dissociation of SO₂ should occur on Pd and Pt surfaces. It was suggested that the interpretation of experimental results be reexamined [74]. The data in Table 24 clearly indicate that the dissociation of SO₂ is facilitated by the presence of CO as a coadsorbate.

Table 24

<table>
<thead>
<tr>
<th>Metal</th>
<th>SO</th>
<th>SO₂</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{SO}$</td>
<td>$\Delta E^*$</td>
<td>$Q_{SO2}$</td>
</tr>
<tr>
<td>Cu</td>
<td>14</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Ag</td>
<td>9</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>Au</td>
<td>9</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>Ni</td>
<td>17</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>Pd</td>
<td>12</td>
<td>0</td>
<td>23</td>
</tr>
<tr>
<td>Pt</td>
<td>11</td>
<td>2</td>
<td>22</td>
</tr>
</tbody>
</table>

*The subscripts, a and s, indicate ‘asymmetric’ and ‘symmetric’, respectively, see text. The values under the heading $\Delta E_{CO}$ correspond to the SO₂ dissociation barriers in the presence of CO as a coadsorbate. All data are from Ref. [74].
adsorbed species on Cu, Ni, Pt, Pd, but might exist on Ag and Au. The desorption and dissociation of SO on Ag and Au surfaces are projected to be competitive [74]. The barriers to oxidation of SO2 to SO3 are below the desorption barriers of SO2 for several oxygen sources such as atomic oxygen on Ag and Au, and O2, NO, H2O2 and SO on all metals examined [74].

The question of the nature of SO3 and SO4 was addressed with ab initio calculations [142]. It was found that SO3 adsorbed on Ag(111) forms an adsorbate that looks very much like neutral SO3 while SO4 forms an adsorbate that appears to be essentially sulfate [142]. It was estimated that sulfate should be a stable surface species at elevated temperatures, but should decompose to SO2 and atomic oxygen before it desorbs.

The model conclusions are consistent with experimental observations although sometimes different explanations are proposed based on the modeling. Some predictions await experimental verification [74].

Since the first UBI-QEP study of SO2 chemistry was published [74], a review of SO2 adsorption on metal surfaces [196] as well as some important experimental works have appeared in the literature [197–199], and we address these new results here. Pangher et al. [197] have studied the structure and decomposition of SO2 on Cu(100) at high coverages of SO2 with X-ray techniques. Among their findings are: (1) SO2 adsorbs with the molecular plane perpendicular to the surface, (2) SO2 is coordinated to the surfaces via the sulfur and at least one oxygen, (3) SO2 decomposition and formation of the (SO2 + O) phase are observed at 180 K, and (4) the formation of the (SO + 2O) phase was reported at 280 K.

The first three points of Pangher et al. [197] enumerated above are consistent with our modeling [74]. However regarding the products of dissociation of SO2, we have indicated that SO2 should not dissociate to SO + O at low coverages, but rather, the dissociation of SO2 along the symmetric path to S + 2O is predicted to be the preferred path on Cu and Ni. Since the work of Pangher et al. [197] corresponds to elevated coverages, we have calculated the heats of adsorption of SO and SO2 and activation barriers for the decomposition and recombination of SO and SO2 as a function of oxygen coverage. The results are summarized in Table 25.

The asymmetric dissociation of SO2 to SO + O is projected to have a prohibitively high activation barrier, and the preferred path for SO2 dissociation is still the symmetric path yielding S + 2O. However, SO becomes a stable surface species between coverages of 0.4 and 0.5 as is indicated by the appearance of the non-zero decomposition barrier. Also, the barrier to S + O recombination decreases

<table>
<thead>
<tr>
<th>θ</th>
<th>QSO2</th>
<th>QSO2</th>
<th>ΔE_d,SO2</th>
<th>ΔE_d,SO2</th>
<th>ΔE_d,SO2</th>
<th>ΔE_d,SO2</th>
<th>ΔE_d,SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>14</td>
<td>30</td>
<td>0</td>
<td>40</td>
<td>21</td>
<td>61</td>
<td>0</td>
</tr>
<tr>
<td>0.4</td>
<td>12</td>
<td>26</td>
<td>0</td>
<td>47</td>
<td>30</td>
<td>46</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>21</td>
<td>7</td>
<td>56</td>
<td>41</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>8</td>
<td>17</td>
<td>13</td>
<td>64</td>
<td>53</td>
<td>23</td>
<td>0</td>
</tr>
</tbody>
</table>

a The dissociation barrier of SO2 along the asymmetric path: SO2 → SO + O.
b The dissociation barrier for SO2 along the symmetric path: SO2 → S + 2O.
c The recombination barrier for: S + O → SO.
d The recombination barrier for: SO + O → SO2.
with increasing coverage. These modeling results are consistent with the appearance of SO at elevated coverages through a two-step mechanism: the symmetric dissociation of SO$_2$ to S + 2O followed by the recombination of S and O. For coverages above about 0.5, SO$_2$ dissociation is probably not a Langmuir–Hinshelwood reaction, since the barrier to symmetric dissociation becomes significantly greater than the desorption barrier in this coverage range. The UBI-QEP heats of adsorption of SO are in disagreement with the claim of Pangher et al. [197] that SO exists on Cu(100) at 280 K. This temperature implies a heat of adsorption greater than 18 kcal/mol and the calculated heat of adsorption of SO varies from 14 to 8 kcal/mol as the coverage ranges from 0 to 0.6. The recombination of SO + O is projected to be diffusion controlled. Because the diffusion barrier of atomic oxygen is 11 kcal/mol on Cu(100), one might expect SO to be observable.

In summary, our modeling projections are in agreement with the presence of SO at elevated coverages. However, as before, these data contradict the assertions [197] that SO exists as a surface adsorbate at 280 K and that SO$_2$ dissociates directly to SO + O.

Zebisch et al. [198] studied SO$_2$ on Pt(110) with TPD, LEED, ARUPS and XPS. Their observations of S, SO$_3$ and SO$_4$ at 340 K are consistent with our modeling [74]. It is noteworthy that they do not report SO as a surface species [198]. The results of Zebisch et al. [198] that SO$_3$ decomposes before it desorbs and that SO$_4$ is stable at elevated temperatures and decomposes to SO$_2$ represents experimental verification of UBI-QEP results [74] which were in the literature a year before the experimental results were published. The high temperature recombinative desorption of atomic S and O to form SO$_2$ mentioned by Zebisch et al. [198] probably occurs via an SO intermediate.

Wilson et al. [199] have carried out TPD, HREELS, XPS and NEXAFS experiments on the SO$_2$/Pt(111) system. Relevant results include: (1) SO$_2$ is di-coordinated via S and O, (2) the plane of the molecule is perpendicular to the surface, (3) the chemistry of SO$_2$ is sensitive to the presence of coadsorbates, (4) CO has a strong influence on the dissociation of SO$_2$ yielding atomic sulfur on the surface, and (5) no SO$_3$ formation was observed up to the desorption temperature of SO$_2$, in contrast to results of Sun et al. [191]. All these points are in agreement with our modeling [74]. In addition, the lack of SO$_3$ formation on Pt(111) was a UBI–QEP modeling prediction [74] that was in conflict with concurrent observations [191] but which is now verified by the new experimental results [199].

9.8. Molecular dynamics simulations of selected dissociation reactions on metal surfaces employing a modified UBI–QEP potential

We employed the NBI potential function of Section 5.1 in the solution of Newton’s equations of motion for O$_2$, S$_2$, C$_2$, N$_2$, and SO on fcc(111) surfaces of Ni, Ag, Au, and Pd. These are the first molecular dynamics simulations to directly yield Arrhenius reaction rate constants (pre-exponentials and activation barriers) for reactions on metal surfaces. Since this is a natural and important extension of the UBI–QEP method, inclusion of this work here is warranted.

To simulate the influence of the zero point vibrational energy, the reactant molecules initially possessed the correct amount of vibrational energy. The $\gamma$ parameter of Section 5.1 was determined in two ways: (a) for reactions in which the UBI–QEP method predicts a zero activation barrier, the Arrhenius barrier (from the slope of an Arrhenius plot) was fit by adjusting the value of $\gamma$ (the UBI–QEP diffusion barrier can be used in the fit when significant); and (b) for reactions having non-zero activation barriers, the barrier was fit by stepping along the minimum-energy reaction path while adjusting $\gamma$ to give a barrier in reasonably good agreement (within 1 kcal/mol) with the
The non-vibrational kinetic energy was split between the translational and rotational degrees of freedom, and simulations at many different ratios were performed. The initial velocity directions for the center of mass motion and the rotational velocity components were varied through a complete set of angles. The simulations were conducted beginning from many initial positions. In all, 256 simulations were conducted for each value of the reactant energy. So, including the averaging over the initial vibrational phase, each Arrhenius plot represents data from 6144 simulations.

Because the center of mass motion of the reactant molecule was unconstrained, the molecule was free to undergo diffusion before dissociation. Therefore, the Arrhenius activation barrier that we obtain from our simulation data is an apparent activation barrier that contains a diffusion contribution. The time per simulation depends on the activation barrier and reactant energy and ranged from a few seconds to several hours of cpu time on our IBM RS6000-580 machines. The algorithm is highly parallelizable.

In unimolecular dissociation reactions, the rate constant is the reciprocal of the average adsorbate lifetime [133,200]:

\[ k = \langle \tau \rangle^{-1}. \]  

(9.8.1)

We carried out the averaging as follows. The initial position and adsorbate energy, \( E_i \), were selected and the velocities of the atoms of the adsorbate and their directions were chosen in such a way as to generate a ‘random’ trajectory sampling without changing the initial reactant energy. The simulations were carried out and the reactant lifetimes were determined. The average reactant lifetime corresponding to the \( i \)-th reactant energy, \( \langle \tau \rangle_i \), is a function of the reactant energy and is the simple arithmetic average of the adsorbate lifetimes. One might think of the set of simulations for a specific reactant energy as composing a microcanonical ensemble. The subsequent average over the set of microcanonical ensembles is:

\[ k = \frac{\sum_{i=1}^{m} \langle \tau \rangle_i^{-1} \exp\{-E_i/k_bT\}}{\sum_{i=1}^{m} \exp\{-E_i/k_bT\}}, \]  

(9.8.2)

where \( k_b \) is the Boltzmann constant, \( m \) is the number of microcanonical ensembles, \( T \) is the absolute temperature and \( E_i \) is the \( i \)-th reactant energy, which is also the energy of the \( i \)-th microcanonical ensemble. A useful expression for the infinite temperature limit of the rate constant, which can be interpreted as the Arrhenius pre-exponential factor, is

\[ k_\infty = \frac{1}{m} \sum_{i=1}^{m} \langle \tau \rangle_i^{-1}. \]  

(9.8.3)

This expression is valuable for those cases in which the activation barrier is significant and therefore the simulation time is long for the low energy reactions. The low energy reactants, which have the longest lifetimes, contribute the least to the infinite temperature limit rate constant.

We employed the atomic and molecular parameters given in Tables 26 and 27 in our MD simulations of the dissociations of \( \text{O}_2 \), \( \text{S}_2 \), \( \text{C}_2 \), \( \text{N}_2 \) and \( \text{SO} \) on fcc(111) surfaces of Ni, Ag, Au and Pt. In the discussion below, the \( \text{O}_2 \) dissociation serves as a representative and pedagogical example. It is also unique among the diatomics we studied in that there is an experimentally determined rate constant [201] with which we compare our calculated values.

Fig. 13 is the Arrhenius plot of the natural logarithm of the rate constant, Eq. (9.8.2), as a function of reciprocal temperature for the dissociation of \( \text{O}_2 \) on Ag(111).
Table 26
Atomic potential energy parameters employed in molecular dynamics simulations of diatomic dissociation reactions

<table>
<thead>
<tr>
<th>Adsorbate/metal</th>
<th>G1</th>
<th>G2</th>
<th>μ1</th>
<th>μ2</th>
<th>aA</th>
<th>R0</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/Ni(111)</td>
<td>1.060 (-1)</td>
<td>1.931 (-2)</td>
<td>1.030 (-2)</td>
<td>1.43142</td>
<td>0.98</td>
<td>2.302</td>
</tr>
<tr>
<td>O/Pt(111)</td>
<td>5.802 (-2)</td>
<td>5.836 (-3)</td>
<td>8.200 (-2)</td>
<td>0.26049</td>
<td>0.66 b</td>
<td>3.685 b</td>
</tr>
<tr>
<td>O/Ag(111)</td>
<td>6.252 (-2)</td>
<td>5.460 (-3)</td>
<td>5.649 (-2)</td>
<td>0.25628</td>
<td>0.66 b</td>
<td>3.685 b</td>
</tr>
<tr>
<td>O/Au(111)</td>
<td>5.972 (-2)</td>
<td>5.475 (-3)</td>
<td>5.557 (-2)</td>
<td>0.26328</td>
<td>1.17</td>
<td>3.650</td>
</tr>
<tr>
<td>C/Ni(111)</td>
<td>1.574 (-1)</td>
<td>2.870 (-2)</td>
<td>1.030 (-2)</td>
<td>1.40842</td>
<td>0.83</td>
<td>3.230</td>
</tr>
<tr>
<td>S/Ni(111)</td>
<td>1.031 (-1)</td>
<td>1.880 (-2)</td>
<td>1.030 (-2)</td>
<td>1.43040</td>
<td>1.27</td>
<td>2.693</td>
</tr>
<tr>
<td>N/Ni(111)</td>
<td>9.492 (-2)</td>
<td>9.460 (-3)</td>
<td>6.668 (-2)</td>
<td>0.2705</td>
<td>0.689</td>
<td>3.000 b</td>
</tr>
</tbody>
</table>

All quantities are in atomic units and are employed in Eqs. (5.6)-(5.9) and (G.5).

b Values have been estimated or assumed.

Table 27
Molecular potential energy parameters and Arrhenius reaction rate constants for the dissociation of the indicated diatomic

<table>
<thead>
<tr>
<th>Molecule/Metal</th>
<th>Molecular parameters</th>
<th>Rate constant a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ</td>
<td>β</td>
</tr>
<tr>
<td>16O2/Au(111)</td>
<td>11.0</td>
<td>1.80</td>
</tr>
<tr>
<td>16O2/Ag(111)</td>
<td>9.5</td>
<td>1.81</td>
</tr>
<tr>
<td>16O2/Pt(111)</td>
<td>9.5</td>
<td>1.71</td>
</tr>
<tr>
<td>16O2/Ni(111)</td>
<td>4.0</td>
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</tr>
<tr>
<td>17O2/Ni(111)</td>
<td>4.0</td>
<td>1.77</td>
</tr>
<tr>
<td>18O2/Ni(111)</td>
<td>4.0</td>
<td>1.77</td>
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<tr>
<td>36S2/Ni(111)</td>
<td>4.0</td>
<td>1.40</td>
</tr>
<tr>
<td>32S16O/Ni(111)</td>
<td>3.9</td>
<td>2.3</td>
</tr>
<tr>
<td>14N2/Ni(111)</td>
<td>17</td>
<td>1.75</td>
</tr>
</tbody>
</table>

The rate constant is defined by \( k = \text{A} \exp\{-\Delta E'/RT\} \).

b Ref. [125]. Energy units are kcal/mol. Arrhenius barriers are rounded off to the nearest 0.1 kcal/mol.

c Ref. [125]. Distances in Bohr.

d Reciprocal seconds. The number in parentheses indicates a multiplicative factor of 10 raised to the power in parentheses.

The Arrhenius rate constant that we obtain from a linear fit to the graphed data is

\[ k = 1.14 \times 10^{12} \text{ s}^{-1} \exp\{-4.3 \text{kcal/mol}/RT\}. \quad (9.8.4) \]

The UBI-QEP intrinsic activation barrier is 4 kcal/mol.

The temperature range employed here may seem high, but, a barrier of 4 kcal/mol is 2013 K so a surface reactant molecule with less thermal energy than this will not react. Also, the temperatures in Fig. 13 correspond to the simulation temperature of the surface O₂, which should not be confused with a physical temperature of a gas phase. Remember that the surface adsorbate is initially hotter than the earlier gas-phase molecule by the heat of adsorption, which on Ag is about 10 kcal/mol [202] or about 5000 K.
The calculated Arrhenius pre-exponentials given in Table 27 all fall in the range that one expects for these types of reactions, namely $10^{11}$–$10^{13}$. The reactions having higher activation barriers tend to have lower pre-exponentials. Also, there is a tendency for the more massive molecules to have lower dissociation pre-exponentials.

The effect on the rate constant of low, but finite, coverage can be taken into account in MD simulations by applying to the NBI $q$ function (employed in Eq. (5.8) and defined in Eq. (G.5)) the UBI–QEP scale factor for the desired coverage, followed by readjustment of $\gamma$ to reproduce the UBI–QEP coverage dependent barrier. We have done this for the case of $O_2$ dissociation on Pt(1 1 1). For a coverage of $\theta = 0.4$, the UBI–QEP scale factor is 0.95 and the UBI–QEP activation barrier is 5.8 kcal/mol. Our rate constants for the dissociation of $O_2$ on Pt(1 1 1) at $\theta = 0$ and $\theta = 0.4$ are, respectively, $k = 5.42 \times 10^{12} \text{s}^{-1} \exp\{-1.1 \text{kcal/mol}/RT\}$, and $k = 7.43 \times 10^{11} \exp\{-5.8 \text{kcal/mol}/RT\}$. These two calculated rate constants bracket an experimental value [201] of $9 \times 10^{11} \text{s}^{-1} \exp\{-2.5 \text{kcal/mol}/RT\}$ that was determined for a low but unknown coverage.

9.9. Applications of the UBI–QEP method by other authors

Since the last review [39] several authors have applied the UBI–QEP method to a variety of chemical problems. For example, Khanra [203] applied the UBI–QEP method to the dissociation of $H_2$, $O_2$ and CO on metallic nanostructures; Tetenyi [204] studied cyclohexane dehydrogenation and ethane
hydrogenolysis on Ni; Rudd and Dumesic \[205\] studied hydrogenolysis of ethane on Ir, Pt, Pd and Co surfaces; Liu and Vannice \[206\] applied the UBI-QEP method to the chemistry of acetone on Pt; Schoofs et al. \[207\] examined the dissociative adsorption of methane on Pt, Ni, Ir, W and Fe; Tao et al. \[208\] applied the UBI-QEP method to PX\(_3\), X = H, Cl, F, CH\(_3\) molecules; Huntley \[209\] has studied the chemistry of H\(_2\)S on Ni, and, Rodrigues has examined CH\(_3\)O, CH\(_3\)S on Cu \[210(a)\] and HS, CH\(_3\)S and C\(_6\)H\(_5\)S on Mo \[210(b)\].

Inevitably, there are misunderstandings, misapplications, and simply wrong statements regarding the UBI-QEP (BOC-MP) method in the literature, and the recent text by Masel \[211\] is remarkable in this respect. This text contains a broad exposition of the UBI-QEP (BOC-MP) method, its fundamental origins and links to other theoretical approaches to chemical reactivity (by Polanyi, Marcus, Tamaru et al.). Unfortunately, while doing so, particularly in his applications of the UBI-QEP method, Masel made quite a number of statements that are without merit. It would be impractical to discuss them all, so we will address only the most misleading and often repeated statements.

A general misunderstanding is the claim \[211\] that the two-body interactions employed in the UBI-QEP (BOC-MP) method are described just by Morse potentials. In reality, the interaction potentials are much more general, as clearly shown in Section 3.

Another general problem in Masel’s work is that in most of his applications of the UBI-QEP (BOC-MP) method, he does not cite explicitly all the appropriate experimental data used, both Q and \(\Delta E^*\), and their published sources, which makes it impossible to verify the validity of his claims. Additional uncertainty and confusion have been created by his use of heats of formation of metal oxides as though these quantities were atomic oxygen chemisorption energies.

Certainly, Masel is incorrect in his major assertion \[211\] that the UBI-QEP (BOC-MP) method is limited in its applicability to disproportionation reactions in which a hydrogen or oxygen (but not nitrogen or carbon) atom is moved from one adsorbate to another. The track record of the UBI-QEP method, which is summarized herein and in Refs. \[38,39\], for dissociation and recombination as well as other types of disproportionation reactions including a wide variety of atoms (including N and C) and atom groups, stands in direct contradiction to Masel’s assertion \[211\].

Similarly, Masel makes a general claim \[211\] that the UBI-QEP (BOC-MP) method ‘works less well’ for different faces of the same metal. In fact, as seen above, when reliable experimental heats of adsorption are known and used for different faces, the UBI-QEP method makes reliable predictions of activation barriers.

Next, Masel contends \[211\] that the UBI-QEP (BOC-MP) method is ‘often not useful in distinguishing between various reaction paths’. The single example that Masel discusses in support of this statement is two possible reactions between adsorbed methanol and oxygen, namely

\[
\text{CH}_3^{16}\text{OH} + ^{18}\text{O} \rightarrow \text{CH}_3^{16}\text{O} + ^{18}\text{OH} \quad (9.9.1)
\]

\[
\text{CH}_3^{16}\text{OH} + ^{18}\text{O} \rightarrow \text{CH}_3^{18}\text{O} + ^{16}\text{OH} \quad (9.9.2)
\]

These two reactions differ in that the first is a hydrogen transfer from methanol to adsorbed atomic oxygen and the second is a methyl group transfer from methanol to atomic oxygen. It has been found that on Ag(110) and Cu(110), reaction (9.9.1) readily occurs but reaction (9.9.2) does not \[212\]. Masel claims this as a failure of the UBI-QEP (BOC-MP) method because it allegedly projects a lower activation barrier for reaction (9.9.2) because the C–O bond is weaker than the O–H bond (see Table 3).
Masel’s claim stems from a typical misapplication. In order to judge the reactivity, one should compare activation barriers, in particular the UBI-QEP ones, only for reactions where the pre-exponential factors are (expected to be) comparable or at least not dramatically different (see, e.g., the discussion of the rate determining step in the ammonia synthesis in Section 9.6). At first sight, both reactions look like similar disproportionation reactions, when the alcohol proton, H, or methyl group, CH$_3$, is transferred to oxygen, $^{18}$O. In fact, it is likely that only reaction (9.9.1) is an elementary reaction and proceeds in a smooth, concerted way through the transition state CH$_3$ $^{16}$O–H–$^{18}$O. By contrast, in reaction (9.9.2), the H atoms in CH$_3$ prevent $^{18}$O from approaching the C atom making the H$_3$C–$^{16}$O bond cleavage (or substantial weakening) a prerequisite. Thus, reaction (9.9.2) may be not elementary or at least would require quite a crowded transition state, so the pre-exponential factor for the rate constant of reaction (9.9.2) as a single, elementary reaction should be much smaller. With a sufficiently low rate constant (pre-exponential), reaction (9.9.2) would more rapidly occur as a ‘non-elementary’ two-step process. An additional kinetic influence, favoring reaction (9.9.1), is that the frequency of the O–H bond vibration is much higher than that of the C–O bond, so the O–H bond has more opportunities to dissociate in a given amount of time.

Indeed, our molecular dynamics simulations [99] confirmed that reaction (9.9.1) is preferred, not because of the relative magnitudes of the dissociation barriers, but because the pre-exponential factor in the rate constant of reaction (9.9.1) is much larger. Sellers [99,112] has found an analogous pattern in the case of methanethiol, CH$_3$SH, in which case the S–H bond cleaves more readily than does the C–S bond despite the fact that the C–S bond is weaker (see Table 3).

10. Comparisons with other theoretical approaches

There are countless quantum mechanical calculations of various adsorbate systems. Until recently, most of the calculations have been done by simple semi-empirical methods, particularly by the extended Hückel method [30] and its modified versions such as the ASED-MO method [213]. In skillful hands and with known basic experimental data, the methods produced reasonable qualitative explanations and projections (see for example Refs. [214–221]). Numerical results of routine calculations, however, much too often were inconsistent with experiment and/or failed to be corroborated by more accurate techniques.

10.1. Chemisorption within first-principle frameworks

With the advent of powerful computers and development of more refined techniques, the sophistication and accuracy of calculations are increasing. Particularly fast growing is the area of density functional (DF) calculations [11–16]. As stressed in Section 1, although the DF theory is in principle exact, its practical accuracy is determined by that of the exchange–correlation potentials, which are not known a priori and therefore their analytical form must be assumed [11–16]. The most common approximation is the local density functional (LDF) [11–16]. The LDF theory is a remarkably efficient structural tool for calculating bond lengths and angles, vibrational frequencies, charge moments, etc. It is not a good thermochemical tool, however, strongly overestimating gas-phase bond energies and especially adsorption energies, typically by tens of kcal/mol [15,16]. Various corrections to the exchange–correlation potentials, introducing local spin-density gradients and incorporating non-local
effects, have significantly improved the calculated thermochemistry of gas-phase molecular processes, where average bond energy errors have sometimes been reduced to several kcal/mol [14–16]. Unfortunately, this level of accuracy is still unreachable for chemisorption energies of atoms and particularly molecules, as we illustrate below.

In general, the more accurate the treatment, the smaller the system treated. First-principles calculations, either ab initio or DFT, as cited in a recent review [35], so far are limited to a few small adsorbates, specifically atoms such as H and O and molecules such as OH, H2O, CO, CHx, OCH3, SCH3, and most recently SO4− [142], HSO− and H2SO4 [140]. The majority of work have been devoted to adsorption and dissociation of a hydrogen molecule on various metal surfaces [35,40,41]. These processes have been studied in great detail, employing both static and dynamic approaches [35,40,41]. It is not clear, however, which features of hydrogen surface chemistry can be transferred to other atoms and molecules. For this reason, we do not discuss the hydrogen studies but move to more complex systems.

Since the UBI-QEP method considers the atomic adsorption energies (for hollow coordination sites) as given and simply takes them from experiment or appropriate theoretical calculations, we focus on the molecular adsorbate energetics, particularly on the heats of adsorption and reaction activation barriers. We see how these important quantities are obtained by state-of-the-art quantum mechanical calculations, ab initio and DFT, and compare them with the appropriate UBI-QEP values.

We start with heats of molecular chemisorption, Q. For these quantities two aspects of the computational accuracy are relevant: the absolute values of Q in a given coordination site and the relative preference of the site determined by energy differences between various adsorbate coordination sites such as ontop versus bridge versus hollow. For atoms, all theoretical methods, including the UBI-QEP method, project the uniform preference of higher coordination, in agreement with experiment. For molecules, there is no uniform experimental pattern; rather, molecular adsorbates have been found in all coordination sites with small energy differences. As we have seen in Section 4, the UBI-QEP method projects the closeness of molecular binding energies in various coordination sites, and because these small differences are effects of the second-order, basically averages them in calculating the values of Q and ΔE∗. Other methods, however, try to calculate Q for each particular site. It is informative to see how successful those attempts are.

10.2. Example: adsorption of CO on Cu surfaces

Consider recent examples of state-of-the-art DFT [61] calculations of simple diatomic molecules such as CO mono-coordinated via the carbon atom on Cu(1 1 1) and (1 0 0).

Various LDF cluster-type calculations, mimicking the (1 0 0) surface by clusters of different sizes, persistently showed a strong preference for the four-fold hollow site, with the binding energies, in the most accurate calculations, of 38 and 15 kcal/mol for the hollow and ontop sites, respectively [61]. Experimentally, CO adsorbs on the Cu(1 0 0) surface in the ontop site with a binding energy of 16.7 kcal/mol [62]. The three-fold hollow site on clusters mimicking the Cu(1 1 1) surface showed even larger overbinding, up to 69 kcal/mol [61] compared to the experimental value of 12 kcal/mol for the ontop site [222]. It was concluded that a major drawback of the LDF cluster calculations is that they give a strong preference for the wrong site [61].

In order to rectify this drawback as well as poor convergence of chemisorption energies with the cluster size, te Velde and Baerends [223] have performed slab LDF calculations of CO on Cu(1 0 0).
The energy convergence with the number of substrate layers was good but the overbinding of CO was still large (≈ 18 and 22 kcal/mol for the ontop and hollow sites, respectively) and the wrong preference for the hollow site remained.

It appears that one should go beyond the local DF approximations. In a later and comprehensive work [61], van Daelen et al. have performed DF calculations of clusters mimicking CO dissociation on Cu(1 1 1) and (1 0 0) surfaces. The authors used the local DF approximations to determine the fully optimized geometries of the reactant, product, and transition states, the energies of which have been calculated within both the local and nonlocal DF approximation (LDA and NLDA, respectively). The cluster size varied between 5 and 50 atoms.

As is common for LDF calculations, the calculated values for the structural properties such as the adsorbates height, the C–O bond length, and the vibrational frequencies were found to rapidly converge with the cluster size and be in good agreement with experiment (this is also true of wavefunction-based ab initio calculations). At the same time, the chemisorption energies proved to be rather sensitive to the cluster structure and the computational approximations.

The ontop coordination energies have been determined for Cu$_x$ clusters with $x = 5, 7, 10$ and 43 for Cu(1 1 1) and for $x = 13$ and 50 for Cu(1 0 0) [61]. For the Cu(1 1 1)-type clusters, the LDA and NLDA binding energies for the ontop site were within the range 19.5–26.0 and 1.4–9.1 kcal/mol, respectively, compared to the experimental value of 12.0 kcal/mol [222]. For the largest Cu cluster, Cu$_{43}$, the LDA and NLDA binding energies were 21.6 (strongly overbound) and 4.3 kcal/mol (strongly underbound), respectively. For the Cu(1 0 0)-type clusters, the LDA and NLDA binding energies for the ontop site were within the range 25.8–34.4 and 6.7–15.6 kcal/mol, respectively, compared to the experimental value of 16.7 kcal/mol [224]. For the largest Cu cluster, Cu$_{50}$, the LDA and NLDA binding energies were 34.4 (strongly overbound) and 15.6 kcal/mol (accurate), respectively.

The hollow site coordination energies have been calculated for clusters of different sizes, which prevents direct comparisons [61]. Here, the largest Cu(1 1 1)-type cluster was Cu$_{31}$ with the NLDA binding energy of 11.5 kcal/mol, which exceeds any of the ontop binding energies cited above and thus predicts the preferred hollow site. By contrast, the largest Cu(1 0 0)-type cluster, Cu$_{28}$, had the NLDA binding energy of 4.6 kcal/mol, which is smaller than the ontop binding energies, so the hollow site appears to be less favorable. The LDS results showed the same trends. As van Daelen et al. [61] concluded, oscillations in the binding energy resulting from cluster size effects are so large that they preclude predictions of the relative stability of the sites. In wavefunction based ab initio calculations these oscillations may be controlled, as Siegbahn and co-workers [144] have shown, by choosing suitably ‘prepared’ bonding states for the clusters, which are usually not the ground electronic state of the cluster. Since the DF methods are applicable only to the lowest energy states of a particular irreducible representation, these binding energy oscillations with cluster size are often an inherent feature of the DFT.

The major thrust of the study [61], however, was the calculation of the reaction enthalpies and activation barriers for CO dissociation. Below we compare some NLDA results [61] with the appropriate UBI–QEP ones with an emphasis on the complementary nature of the two approaches.

Remember that the UBI–QEP method makes use of the heat of atomic chemisorption $Q_A$ as an input parameter. In particular, in order to calculate the binding energy of CO mono-coordinated via the C atom, we need the value of $Q_C$. Of the four possible binding energies of two atoms (C and O) on two metal surfaces (Cu(1 1 1) and Cu(1 0 0)), the only known experimental value is for $Q_O$ on a polycrystalline Cu surface which is close to Cu(1 1 1), namely 103 kcal/mol [225]. Lacking the
experimental data, the best alternative is to borrow the values, $Q_A$, from appropriate theoretical calculations, particularly from the NLDA ones which appear to be most accurate for atomic binding energies.

van Daelen et al. [61] considered the CO dissociation from the reactant state (RS) of CO in the hollow site, regardless of its energetic preference, through various assumed transition states (TS) to the dissociated state (DS), where the adatoms C and O occupy the hollow sites of adjacent meshes sharing one or two metal atoms. The DS with one shared metal atom is always more favorable energetically, and the appropriate DS binding energy, which we denote as $(Q_C + Q_O)_M$, is 193 kcal/mol for Cu(1 1 1) (for the largest cluster, Cu$_{131}$) and 217 kcal/mol for Cu(1 0 0) (for the largest cluster, Cu$_{28}$). Within the UBI–QEP method, coordination of adatoms sharing a metal atom is not a ground DS; the latter corresponds to the coordination with no shared metal atoms (adatoms occupying hollow sites in non-adjacent meshes). The relevant correction can be calculated via Eq. (60) in Ref. [38] which takes into account the coverage effect resulting from sharing by two adatoms, A and B, one metal atom. Because the value of $Q_C$ is apparently close to $Q_O$, one can use the simpler Eqs. (52) and (53) in Ref. [38] (or Eq. (4.8.2) of Section 4.8) which gives the ground state values $Q_C + Q_O$ of around 193/0.917 = 210 kcal/mol for Cu(1 1 1), $\theta = 2/5$, and 217/0.938 = 230 kcal/mol for Cu(1 0 0), $\theta = 2/7$. For Cu(1 1 1), taking the experimental value of $Q_O = 103$ kcal/mol, we estimate $Q_C = 107$ kcal/mol. Assuming the same ratio of $Q_O/Q_C = 103/107 = 0.963$ as for Cu(1 1 1), we predict for Cu(1 0 0) the values of $Q_O = 113$ kcal/mol and $Q_C = 117$ kcal/mol.

The appropriate UBI–QEP binding energies of CO (via Eq. (4.2.1.3)) on Cu(1 1 1) and (1 0 0) are 12 and 14 kcal/mol, respectively. Of course, the above estimation procedure is not unique, but other reasonable estimates are still within the rather narrow range of $Q_C = 105–115$ kcal/mol for Cu(1 1 1) and 110–125 kcal/mol for Cu(1 0 0), which leads to the range of $Q_{CO}$ of 12–14 and 13–17 kcal/mol, respectively, in good agreement with the appropriate experimental values of 12 [222] and 17 kcal/mol [224]. Perhaps, very good agreement may not be desirable because the experimental data were obtained more than two decades ago. The results are summarized in Table 28.

For CO dissociation and recombination, the reaction enthalpies, $\Delta H_{\text{dis}}$, and intrinsic activation barriers, $\Delta E_{\text{dis}}^*$ and $\Delta E_{\text{rec}}^*$, calculated by the NLDA and UBI–QEP methods are shown in Table 29. Quantitatively, the UBI–QEP values of $\Delta H$ and $\Delta E^*$ are distinctly smaller, but there are no direct experimental data to verify the numbers. Qualitatively, both methods make similar projections, specifically, that CO dissociation is highly endothermic on both Cu(1 1 1) and Cu(1 0 0) with the latter being less endothermic, and that CO should desorb before dissociation because $Q_{CO} \ll \Delta E_{\text{dis}}^*$, in agreement with the experiment. An important difference between the predictions of the two methods is that, on Cu(1 1 1), the UBI–QEP intrinsic C + O recombination barrier is zero (compared with the DFT barrier of 23 kcal/mol). As discussed in Section 4, the apparent non-zero barrier should be due to mutual C and O diffusion and of a magnitude of around 10 kcal/mol (cf. Eq. (4.7.2.2)). By the same token, the diffusional contribution may also be important for Cu(1 0 0) where the intrinsic recombination barrier of 9 kcal/mol appears to be smaller than the diffusional barrier of 12 kcal/mol (cf. Eq. (4.7.2.6)). The lack of the intrinsic activation barrier for highly exothermic recombination reactions is a common UBI–QEP prediction which indicates the necessity of inclusion of the diffusional contribution.

Te Velde and Baerends [223] have studied coverage effects on the CO binding energy, and infrared reflection adsorption spectroscopy (IRAS) studies of CO on Pt and Ni surfaces [226,227] have been conducted. One of the important conclusions of the te Velde and Baerends [223] study was that the low
Table 28
UBI–QEP energetics (kcal/mol) of CO chemisorption and dissociation on Cu surfaces

<table>
<thead>
<tr>
<th>Entity</th>
<th>Cu(1 1 1)</th>
<th></th>
<th>Cu(1 0 0)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Q_c + Q_o)_M$</td>
<td>193</td>
<td>a</td>
<td>217</td>
<td>a</td>
</tr>
<tr>
<td>$Q_c + Q_o$</td>
<td>210</td>
<td>b</td>
<td>230</td>
<td>b</td>
</tr>
<tr>
<td>$Q_o$</td>
<td>103</td>
<td>c</td>
<td>113</td>
<td>e</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>107</td>
<td>d</td>
<td>117</td>
<td>e</td>
</tr>
<tr>
<td>$Q_{oc}$</td>
<td>64</td>
<td></td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>$Q_{co}$</td>
<td>12</td>
<td>12.0</td>
<td>14</td>
<td>16.7</td>
</tr>
<tr>
<td>$\Delta H_{dis}$</td>
<td>59</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$\Delta E_{dis}^*$</td>
<td>59</td>
<td></td>
<td>49</td>
<td></td>
</tr>
</tbody>
</table>

a The NLDA values for the adatoms C and O in the hollow sites of adjacent meshes sharing one metal atom [61].
b The NLDA values for the adatoms C and O in the hollow sites of non-adjacent meshes corrected via Eq. (4.8.2).
c The experimental value, see [225].
d The corrected NLDA value (cf. b and c).
e The estimated values assuming the same ratio of $Q_o/Q_c = 0.963$ as for Cu(1 1 1).
f Ref. [222].
g Ref. [224].

Table 29
Calculated reaction enthalpies, $\Delta H$, and activation barriers for dissociation, $\Delta E_{dis}^*$ and recombination, $\Delta E_{rec}^*$ (kcal/mol) for CO on Cu surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>NLDAb</th>
<th>$Q_{CO}$</th>
<th>$\Delta H_{dis}$</th>
<th>$\Delta E_{dis}^*$</th>
<th>$\Delta E_{rec}^*$</th>
<th>UBI–QEPb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_{CO}$</td>
<td>$\Delta H_{dis}$</td>
<td>$\Delta E_{dis}^*$</td>
<td>$\Delta E_{rec}^*$</td>
<td>$Q_{CO}$</td>
</tr>
<tr>
<td>Cu(1 1 1)</td>
<td>12</td>
<td>85</td>
<td>108</td>
<td>23</td>
<td>12</td>
<td>59</td>
</tr>
<tr>
<td>Cu(1 0 0)</td>
<td>5</td>
<td>54</td>
<td>85</td>
<td>31</td>
<td>14</td>
<td>40</td>
</tr>
</tbody>
</table>

a All data from Ref. [61]. The values of $Q_{CO}$ for the hollow sites were used for calculating $\Delta H_{dis}$ and $\Delta E_{dis}^*$. See comments in text.
b See Table 28 and comments in the text.

adsorption energy at complete coverage is not due to direct CO–CO steric interactions, but must be caused by “through lattice” electronic effects of neighboring Cu–CO bonds, which are rather small for coverages $\leq 0.5$ ML. In this respect, one can mention that the IRAS study of CO on Pt(1 1 1) and Ni(1 0 0) at very low temperatures of 18–25 K and at low coverages of 0.003–0.15 ML provided experimental evidence of substantial substrate-mediated interaction between adsorbed CO molecules operating at a relatively long range of $> 10 \text{Å}$ [226]. Recall that in the UBI–QEP method, coverage effects on chemisorption energies are explicitly of the surface-mediated origin (see Section 4).

10.3. Example: adsorption of CH$_4$ on Ni surfaces

From all carbon-containing adsorbates on metal surfaces, nickel is uniquely appropriate for the UBI–QEP analysis because only for Ni(1 1 1) and Ni(1 0 0) [123] surfaces are the experimental values of $Q_C$
Table 30
Calculated and experimental heats of adsorption (kcal/mol) of CH₄ species

<table>
<thead>
<tr>
<th></th>
<th>Ab initio</th>
<th>NLDA</th>
<th>UBI–QEP</th>
<th>Exp c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni₁</td>
<td>Ni₁₃</td>
<td>Ni₁</td>
<td>Ni₁₃</td>
</tr>
<tr>
<td>CH₃</td>
<td>49</td>
<td>41</td>
<td>23</td>
<td>43</td>
</tr>
<tr>
<td>CH₂</td>
<td>88</td>
<td>67</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>CH</td>
<td>120</td>
<td>72</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>C</td>
<td>134</td>
<td>142</td>
<td>58</td>
<td>65</td>
</tr>
<tr>
<td>H</td>
<td>62</td>
<td>62</td>
<td>63</td>
<td>63</td>
</tr>
</tbody>
</table>

a For the CH₄ gas-phase ground state geometry, these values should be decreased by 8 (CH₃) and 6 (CH₂) kcal/mol [64].

b Assumed value for calculating the heats of CH₄ adsorption.

See Ref. [39] for discussion of methane chemisorption energy and Table 1 for atomic binding energy references.

known. Of various surface reactions, dissociation of CH₄ on Ni(1 1 1) has drawn particular interest and has been treated by different theoretical methods, including ab initio, DFT, and UBI–QEP.

Consider first calculations of the heat of adsorption of CH₃ on Ni(1 1 1) [35] for the purpose of determining the binding site preference. The only experimental datum is the surface-CH₃ stretch frequency, which is 370 cm⁻¹ [228]. Although some authors claim [64] that this value is indicative of the preferred ontop site, the assignment is far from definitive. (One of the latest examples of wrong site assignments based on vibrational frequencies is the chemisorption geometry of NO on Rh(1 1 1) which, by considerations of vibrational frequencies, was assigned as two-fold bridge, but, by other and more direct techniques, proved to be ontop and hollow [229].) The NLDA cluster-type calculations by Burghgraef et al. [62–65] strongly prefer the ontop site but the NLDA slab calculations by Kratzer et al. [230] as well as ab initio cluster-type calculations by Schule et al. [231] and by Yang and Whitten [35] prefer the hollow site. Table 30 summarizes these data for CH₄ species.

The reaction CH₄,g → CH₃,s + Hₚ on Ni(1 1 1) is perhaps the most complex system studied by the ab initio and DFT methods. The ab initio calculations were cluster-type [232] and the DFT calculations were both cluster and slab-type [61,63,64,233]. The results were very sensitive to the cluster (mesh) size and geometry of the assumed reaction path. As shown in Section 9.1, the reaction has also been treated by the UBI–QEP method as the simplest case of the FT synthesis. The appropriate data are summarized in Table 31.

Unfortunately, there are no quantitative experimental data on the reaction enthalpy and activation barrier but only qualitative observations and some indirect measurements concerning dissociation of CH₄ on Ni surfaces leading to a variety of CH₃ products [228,234–245]. In particular, only the apparent activation barrier for thermal dissociation of CH₄ on Ni(1 1 1) has been measured and found to be 12–13 kcal/mol [228,237]. But if dissociation of a polyatomic molecule does not stop at the first dissociation step, the process includes several successive bond scissions resulting in a variety of products from various elementary steps. Thus, the measured apparent activation barrier may not be directly related to any particular elementary step, although this barrier may be assumed to be not larger than that for the first bond dissociation. As seen from Table 31, only the UBI–QEP barrier is consistent with this assumption.
Table 31
Calculated enthalpy and activation barrier (kcal/mol) of the reaction \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) on Ni(1 1 1)

<table>
<thead>
<tr>
<th></th>
<th>Ab initio</th>
<th>DFT</th>
<th>UBI-QEP</th>
<th>Exp (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref. [231]</td>
<td>Ref. [64]</td>
<td>Ref. [230]</td>
<td></td>
</tr>
<tr>
<td>( \Delta E_{diss} )</td>
<td>17</td>
<td>51</td>
<td>29</td>
<td>8</td>
</tr>
<tr>
<td>( \Delta H_{diss} )</td>
<td>-6</td>
<td>-3</td>
<td>34</td>
<td>-6</td>
</tr>
</tbody>
</table>

\(^a\) The apparent activation barrier for dissociation of \( \text{CH}_4 \) (see text).
\(^b\) Ref. [237].
\(^c\) Ref. [123].

Table 32
Calorimetric initial heats of CO adsorption (kcal/mol) on selected Ni, Pd and Pt surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>( Q_{\text{CO}} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1 1 1)</td>
<td>43</td>
<td>[249]</td>
</tr>
<tr>
<td>Pt(1 0 0)</td>
<td>(1 x 1)</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>(hex)</td>
<td>43</td>
</tr>
<tr>
<td>Pt(1 1 0)</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Pd(1 0 0)</td>
<td>(1 x 1)</td>
<td>39</td>
</tr>
<tr>
<td>Ni(1 1 1)</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Ni(1 0 0)</td>
<td>(1 x 1)</td>
<td>29</td>
</tr>
<tr>
<td>Ni(1 1 0)</td>
<td></td>
<td>32</td>
</tr>
</tbody>
</table>

10.4. The M–CO bonding: within or beyond the scope of the UBI–QEP method

We stressed before that the nature of chemisorption M–CO bond can be determined only by high-quality first-principle calculations. For 3d metals such as Ni and Cu, such calculations have been made [118], in good agreement with experiment [118]. For 4d and particularly 5d metals, such as Pt, no high-quality calculations exist, so the nature of Pt–CO bonding is still a matter of qualitative speculation.

Experimental values of CO adsorption energies are available for various metal surfaces, mostly from TPD data but recently from direct calorimetric measurements [246–251]. The calorimetric data on \( Q_{\text{CO}} \) for major metal surfaces of Ni, Pd and Pt are given in Table 32.

Since experimental values of atomic carbon binding energy are known only for Ni(1 1 1) and Ni(1 0 0) [252], reliable UBI–QEP values of \( Q_{\text{CO}} \) can be obtained for those surfaces only. Table 33 lists available TPD and calorimetric data on \( Q_{\text{CO}} \) on Ni(1 1 1) and Ni(1 0 0) as well as results of UBI–QEP calculations. The agreement between all the data is excellent, which convincingly demonstrates that the chemisorption Ni–CO bonding is within the scope of the UBI–QEP method.

It may be a different story for the Pd–CO and particularly Pt–CO bonding. Experimental values of \( Q_{\text{CO}} \), both TPD and calorimetric, increase for all comparable surfaces along the series, Ni < Pd < Pt. The increase in the TPD values is within 5 kcal/mol [252] but that for the calorimetric values is even...
Table 33
Experimental (TPD and calorimetric) versus theoretical UBI-QEP heats of CO adsorption (kcal/mol) on Ni surfaces

<table>
<thead>
<tr>
<th>Ni(1 1 1)</th>
<th>Ni(1 0 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>Theory</td>
</tr>
<tr>
<td>TPD</td>
<td>Cal</td>
</tr>
<tr>
<td>27(^a)</td>
<td>31(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Ref. [252(a)].  
\(^b\) See Table 32.  
\(^c\) Eq. (4.2.1.4).  
\(^d\) Ref. [252(b)].

higher. For example, the values of \(Q_{CO}\) on Pt surfaces, as seen from Table 32, exceed those on Ni by 15–20 kcal/mol. Excluding reconstruction effects, the only way for the UBI-QEP method to explain such a large difference is to assume that the atomic carbon binding energies, \(Q_c\), also increase along the series, Ni < Pd < Pt. Although experimental and reliable theoretical information is unavailable, this series would be just reversed to that observed for all other atoms including oxygen and nitrogen. Because the reversed series is not justified, we are inclined to believe that the Pt–CO bonding is beyond the applicability of the UBI-QEP method.

What might the reasons be? The Pt–Pt bonds are unusual in that they exhibit a non-competitive nature as manifest in the non-oscillatory behavior of the near-surface layer spacings (cf. Section 3.1.1). We also pointed out (cf. Section 3.1.3) that, if the donor–acceptor \(\sigma\)-M—C–O bond is significant, the CO adsorption may be beyond the UBI-QEP method. Indeed, some qualitative arguments have been advanced [113] that the donor–acceptor \(\sigma\)-M—C–O bond is predominant and its strength increases along the series, Ni < Pd < Pt. If so, the M–C and C–O bonding may not be competitive and there may be no UBI–QEP correlation between the carbon binding energy and the total M–CO bond energy. High quality ab initio calculations of chemisorption Pt–CO bonding are needed.

11. Concluding remarks

The words of J.W. Gibbs, which we chose as a motto of this review, stress the virtue and value of coherent simplicity in a theoretical construct. In other words, a worthy theoretical model should reveal an organizing principle that makes comprehensible the hidden order of apparently unrelated phenomena. From the start, the UBI–QEP method (then going by the name of BOC–MP) has shown a promise to be an organizing framework of chemisorption on transition metal surfaces, to become an “elephant” model interrelating seemingly disparate phenomena as parts of the whole [38]. The subsequent developments, described in this review, have substantially realized that promise.

The current UBI–QEP method is general, sound, efficient, and practical. It combines an explicit and rigid analytical framework with a fast and easy computational implementation. As input parameters, the method employs a few thermodynamic observables (gas-phase bond energies and atomic chemisorption
energies). Its output is the whole surface reaction energetics (molecular chemisorption energies, reaction enthalpies and activation barriers); and all these for low and higher coverages, on uni- and bimetallic surfaces, for static and dynamic situations. Because the UBI–QEP results are incomparably faster, easier and cheaper to obtain than those of the current ab initio and DFT methods, they are much more diverse and relevant to complex systems of practical interest. Moreover, the UBI–QEP projections of reaction energetics are usually more accurate.

The reader may ask: Are there any cases for which the UBI–QEP method fails? The question requires some clarification of the meaning of failure. The UBI–QEP method is a way to calculate the reaction energetics for a given surface and allows the interpretation of surface reactivity in terms of the energetics only. So, one should distinguish the accuracy of energy calculations from that of the reactivity projections. The more the reactivity is affected by non-energetic contributions, such as the Arrhenius pre-exponential factors which reflect entropy changes along the reaction path and other factors, the more probable that events will not be adequately described by the model. The true test of the UBI–QEP method is how accurately it generates the reaction energetics.

Naturally, the accuracy of the UBI–QEP energetics depends on the size of the system being treated and the accuracy of the thermodynamic input parameters, particularly the $Q_{AS}$. The best defined case corresponds to atoms and small molecules as independent adsorbates under low coverages on unimetallic close-packed surfaces. The least defined case is large adsorbates at high coverages on open bimetallic surfaces. In intermediate cases, the surface structure and the number and size of adsorbates vary between the two extremes. At present, by using the UBI-Model computer program, one can easily estimate coverage effects on both unimetallic and bimetallic surfaces. Moreover, one can reinstate the terms neglected in the standard analytic formalism and further improve the numerical accuracy of individual complex cases. In the best and reasonably well-defined cases, the calculated UBI–QEP energetics are in good quantitative agreement with reliable experimental measurements.

One final comment is appropriate. In general, one may distinguish conceptual/qualitative from numerical/quantitative failure, although the two are certainly related. The quantum mechanical methods cannot fail conceptually because quantum mechanics, by definition, is the only 'true' language of the microworld. When they fail in numbers, as typically they do for large systems, one can always blame technicalities and have another try after modifying various terms in the Hamiltonian, improving the basis set, extending the CI space, etc. That is why there are so many legitimate but practically useless quantum mechanical calculations. By contrast, phenomenological methods, whose first-principles connections might not be clear, cannot afford to be useless. If such a method not only produces accurate enough estimates for a wide variety of entities, but also does it in a transparent, systematic and coherent way, the method's legitimacy is established. The phenomenological UBI–QEP method and quantum mechanical methods are complementary in both the physical nature and the information obtained. The UBI–QEP method deserves a careful look from the practitioners of surface chemistry.

12. Glossary

$D_{AB}$ The gas-phase bond energy of a molecule, AB, which is the enthalpy of the gas-phase reaction: $AB \rightarrow A + B$. Both A and B can be groups of atoms or molecular fragments.
\( D_{iA} \) The bond energy that is internal to a quasi-atomic species. It is the enthalpy required to break the internal bond(s) in the A fragment that connects the contact atom to the rest of the fragment.

\( D \) Diffusivity or the Arrhenius rate constant for diffusion

\( D^s \) Diffusivity of the precursor state. The precursor state is not a transition state

\( k_i \) The number of metal atoms involved in binding to a specific number of adatoms, \( A_m \), in the \( n \)-fold binding site \( \sum_i k_i = n \)

\( L \) The Lagrangian energy function

\( l \) The number of metal atoms of type 1

\( l' \) The number of metal atoms of type 2

\( m_i \) The number of adatoms, A, to which a specific metal atom binds. The subscript refers to a grouping which is termed a ‘local-symmetry’ type or group. The metal atom to which \( m_i \) refers belongs to the \( i \)th local-symmetry group

\( m \) The number of adatoms of type A

\( m' \) The number of adatoms of type B

\( n \) The number of metal atoms that defines a specific binding site. \( n = 1 \) for an ontop site, \( n = 2 \) for bridging site, \( n = 3 \) for the fcc(111) hollow, \( n = 4 \) for the fcc(100) hollow, etc

\( Q_{0A} \) The two-center bond energy, in the zero coverage limit, between a single metal atom of the metal surface and an adsorbate atom A, which relates the atomic binding energy, \( Q_A \), to \( n \) pairwise contributions as: \( Q_{0A} = Q_A / (2 - 1/n) \). \( Q_{0A} \) is also the ontop binding energy since \( Q_{0A} = Q_A \) for \( n = 1 \)

\( Q_{0A}(\theta) \) The coverage dependent two-center bond energy between a single metal atom of the metal surface and an adsorbate atom A

\( Q_0A \) See \( Q_{0A} \) above. The prime is used in the bimetallic formulas to indicate that this quantity refers to the second type of metal atom

\( Q_A \) The maximum atomic binding energy which is the observable atomic heat of adsorption for atom A in the zero coverage limit. See \( Q_{nA} \) below

\( Q_A(\theta) \) The coverage dependent, observable atomic heat of adsorption

\( Q_{nA} \) The atomic binding energy in the \( n \)-fold binding site. This quantity may be a calculated quantity or the result of experimental measurement. \( Q_A \) and \( Q_{nA} \) are related in the sense that \( Q_A \) is the special case of \( Q_{nA} \) when \( n \) takes on its maximum value for a given surface, e.g., \( n = 3 \) for fcc(111) surfaces so that \( Q_A = Q_{3A} \) for fcc(111) surfaces. In this notation, the parameter \( Q_{0A} = Q_{1A} \)

\( Q_{nA}(\theta) \) The coverage dependent atomic binding energy in the \( n \)-fold binding site

\( Q_0(BC) \) This quantity is analogous to \( Q_{0A} \) above and indicates that the molecular fragment, BC, is treated as a pseudo-atom

\( Q_M(m, m') \) The binding energy of a single metal atom to an arrangement of adatoms, \( A_mB_{m'} \). The \( m \) adatoms of type A and \( m' \) adatoms of type B are treated as though they interact only with the metal atom. \( Q_M(m, m') \) is also a function of \( n \)

\( r \) An inter-body distance

\( r_0 \) An equilibrium inter-body distance

\( r_{\text{ref}} \) The reference distance, not necessarily the equilibrium distance

\( x(r) \) The two-body bond index as a function of distance, \( r \)
The bond index between adatom A and an atom of the metal surface. Although it may not always be indicated, all bond indices are functions of a distance variable.

The group bond index. This variable also represents the two-body bond index in cases in which either may be used.

The group bond index between adatom A and the metal surface.

Total bond index.

The interaction index between adatom A and metal surface introduced in the potential energy functions employed in molecular dynamics simulations as an analog of the group bond index $x_A$.

Acknowledgements

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Appendix A. Development of formulas for heats of adsorption

In this appendix we give detailed descriptions of the derivations of the UBI–QEP molecular binding energy formulas on unimetallic surfaces. In these derivations we favor the Lagrangian multiplier technique for constrained optimization. In some cases, however, its use complicates rather than simplifies the derivation, and in such cases the UBI constraint is substituted directly into the energy equation. In our mathematical developments given in this and subsequent appendices, the constraint condition is written so that it contributes to the energy derivatives but not to the energy itself. So the Lagrangian energy function, $L$, and the UBI–QEP energy function, $E$, have the same numeric value.

A.1. Atomic binding

The binding energy of the adatom with the surface in the n-fold binding site is taken to be

$$E = Q_{0A} \sum_i [x_i^2(r_i) - 2x_i(r_i)], \quad (A.1)$$

where the $Q_{0A}$ parameter describes the strength of the two-center M–A interaction and the summation runs from 1 to $n$: $n = 1$ for ontop, $n = 2$ for bridging and $n = 3$ for fcc(1 1 1) hollow. We employ the method of Lagrangian multipliers to optimize the energy, Eq. (A.1), under the constraint of unity bond index, Eq. (3.5.1). The Lagrangian function to optimize is

$$L = E - \alpha \left( \sum_i x_i(r_i) - 1 \right), \quad (A.2)$$
where $\alpha$ is the Lagrangian multiplier of the UBI constraint and the summation runs from 1 to $n$. The optimization is carried out in bond index space and gives the same energy minimum as coordinate optimization as is discussed in Appendix B. Putting the first derivatives of the Lagrangian function to zero results in

$$ \frac{\partial L}{\partial x_k} = 2Q_{0A}(x_k(r_0) - 1) - \alpha = 0 \quad \text{for all } k. \quad (A.3) $$

Solving this equation for the $k$th bond index at the equilibrium distances, $x_k(r_0)$ gives

$$ x_k(r_0) = 1 + \alpha/(2Q_{0A}). \quad (A.4) $$

One solves for $\alpha$ by substituting Eq. (A.4) into the UBI condition, Eq. (3.5.1):

$$ \alpha = 2Q_{0A}(1/n - 1). \quad (A.5) $$

Eqs. (A.5) and (A.4) give the result that

$$ x_k(r_0) = 1/n \quad \text{for all } k. \quad (A.6) $$

The surface binding energy is obtained by substituting (A.6) into (A.1):

$$ Q_{nA} = -E(n) = Q_{0A}(2 - 1/n). \quad (A.7) $$

A.2. Weak, erect binding

The AB molecule is bound with the A atom as the contact atom and atom group B directed away from the surface. Since the bond indices are inverse exponential functions of distance, the M–B interactions are small and are neglected. The UBI–QEP energy expression is

$$ E(n) = Q_{0A} \sum_i (x_{A,i}^2 - 2x_{A,i}) + D_{AB}(x_{AB}^2 - 2x_{AB}). \quad (A.8) $$

The quantity, $D_{AB}$, is the enthalpy of the reaction that breaks the AB bond. In carrying out the constrained optimization we will substitute the constraint into Eq. (A.8) rather than use the Lagrangian multiplier method.

When the contact atom of the adsorbate is in the center of the binding site: $x_{A,1} = x_{A,2} = x_{A,3}$ etc., so that all $n$ terms of the summation are the same. We will assume this symmetry in the development below but there may be cases in which it is not satisfied for polyatomics. For example, while C–CH$_3$ adsorbed in a three-fold hollow may have a $C_3$ axis of rotation that includes the binding site, C–CH$_2$ would not have such an axis and a slight symmetry breaking would be present. However, such a situation causes no significant difference in the binding energy. Also, most of the applications of the weak binding formula that we are developing here are for closed-shell molecules in the ontop site for which the symmetry considerations do not apply. Assuming the contact atom of the adsorbate to be situated in the center of the binding site allows us to write

$$ E(n) = nQ_{0A}(x_{A,1}^2 - 2x_{A,1}) + D_{AB}(x_{AB}^2 - 2x_{AB}). \quad (A.9) $$

The optimization constrained by the UBI condition

$$ nx_{A,1} + x_{AB} = 1 \quad (A.10) $$
is conveniently conducted by solving Eq. (A.10) for $x_{AB}$ and substituting this into Eq. (A.9) followed by putting $dE/dx_{A,1}$ to zero. This gives for $x_{A,1}$ at the chemisorbed minimum:

$$x_{A,1} = \frac{Q_{0A}}{(nD_{AB} + Q_{0A})}. \tag{A.11}$$

Putting these expressions for the equilibrium bond index back into the energy expressions and subtracting the energy of the desorbed AB molecule, $-D_{AB}$, gives for the binding energy:

$$Q_{AB,n} = \frac{Q_{0A}^2}{Q_{0A}/n + D_{AB}}. \tag{A.12}$$

### A.3. Strong, erect binding

Strongly bound surface species behave much like atoms in their preference for binding sites, and so, the potential that describes the interaction between the contact atom and the metal surface is well described by the potential:

$$Q_A(x_A^2 - 2x_A), \tag{A.13}$$

where $x_A$ is the group bond index between the contact atom A and the surface and $Q_A$ is the atomic heat of adsorption. The UBI–QEP energy expression is obtained by adding to this the stretching potential for the AB bond (B can be an atom group):

$$E = Q_A(x_A^2 - 2x_A) + D_{AB}(x_{AB}^2 - 2x_{AB}) \tag{A.14}$$

and the unity bond index condition is

$$x_A + x_{AB} = 1. \tag{A.15}$$

Since there are only two bond indices, we enforce the constraint, (A.15), by substituting (A.15) into (A.14). Putting the derivative $\partial E/\partial x_A$ to zero gives for the chemisorbed equilibrium bond indices

$$x_A = \frac{Q_A}{(Q_A + D_{AB})} \quad \text{and} \quad x_{AB} = \frac{D_{AB}}{(Q_A + D_{AB})}. \tag{A.16}$$

Putting Eqs. (A.16) into (A.14) and subtracting the energy of the desorbed AB molecule, $-D_{AB}$, gives for the binding energy

$$Q_{AB} = -E + D_{AB} = \frac{Q_A^2}{(Q_A + D_{AB})}. \tag{A.17}$$

### A.4. Other two-body interaction potentials

In Section 3.3 we commented that two-body potentials having one non-zero extremum can be constructed by multiplying the right-hand side of Eq. (3.3.2) by $x^n$, which gives Eq. (3.3.8):

$$E = x^n[a_2x^2(r) + a_1x(r)], \quad n > 0. \tag{A.18}$$

In this section we show that this potential can lead to physically unrealistic multiple extrema in the adsorption/desorption potential. We define this potential as describing the interaction energy between a metal surface and an adsorbed, non-dissociated molecule in a well-defined orientation above the surface. We maintain that the adsorption/desorption potential should have one and only one non-zero
extremum. In this discussion we exclude potentials describing adsorption followed by a change in binding site or coordination mode not to mention dissociation. Such potentials obviously may have more than one extremum, and we exclude them as corresponding to non-elementary processes.

Employing the potential of Eq. (A.18), the UBI–QEP potential function for the adsorption/desorption of AB is

$$E = x_A^{n_A} [a_{2A} x_A^2(r) + a_{1A} x_A(r)] + x_B^{n_B} [a_{2B} x_B^2(r) + a_{1B} x_B(r)] + x_{AB}^{n_{AB}} [a_{2AB} x_{AB}^2(r) + a_{1AB} x_{AB}(r)].$$  \(\text{(A.19)}\)

The UBI constraint is

$$x_A + x_B + x_{AB} = 1, \quad x_A = 1 - x_B - x_{AB}. \quad \text{(A.20)}$$

Enforcing the constraint by substituting $x_A$ from Eq. (A.20) into Eq. (A.19) gives

$$E = (1 - x_B - x_{AB})^{n_A} [a_{2A} (1 - x_B - x_{AB})^2 + a_{1A} (1 - x_B - x_{AB})] + x_B^{n_B} [a_{2B} x_B^2(r) + a_{1B} x_B(r)]$$

$$+ x_{AB}^{n_{AB}} [a_{2AB} x_{AB}^2(r) + a_{1AB} x_{AB}(r)].$$  \(\text{(A.21)}\)

From inspection of Eq. (A.21) one sees that the energy function will have a multiplicity of extrema barring fortuitous exceptions due to special-case values of the potential constants. The assumption of the pairwise additivity of the two-body potentials presumes that the two-body interaction potential is fundamental and does not change in differing situations. For a specified pair of entities, there should be a single, correct two-body interaction for all applications. Therefore one should not adjust the two-body potential constants to rid the total energy, Eq. (A.21), of unphysical extrema so as to allow certain values of $n_A$, $n_B$ and $n_{AB}$ in certain cases. In other words, allowing the $a_1$ and $a_2$ parameters to be free of arbitrary constraints, the adsorption/desorption potential will be free of unphysical extrema in all cases if and only if $n_A = n_B = n_{AB} = 0$.

Appendix B. The correspondence between bond index space optimization and coordinate space optimization

The coordinate space optimization and bond index space optimization as employed in the UBI–QEP method usually result in the same energy minimum, and in this section we develop the conditions that must be met for this to be the case. We can proceed in one of two ways. The specific way we choose is dependent on the case at hand. We can employ individual two-center bond indices or group bond indices. For example

$$x_A = \sum_i x_{Ai}.$$  \(\text{(B.1)}\)

defines the group bond index between atom A and the metal surface. The use of group bond indices requires that a single two-body potential expresses the overall interaction, and therefore the related energy parameters are different from those that express the pairwise M–A interactions. Some adsorbates, such as strongly bound diatomic and polyatomic radicals, are naturally amenable to the use of group bond indices because they tend to behave like atoms in that they prefer to bind (erect) in the hollow site.
For a given (diatomic) adsorbate, AB, and given coordination mode and binding site, we construct an energy expression by summing all the pairwise interaction potentials

\[ E = \sum_i Q_i (x_i^2 - 2x_i) + D_{AB} (x_{AB}^2 - 2x_{AB}), \]  

where the \( Q_i \) represent potential parameters yet to be specified, \( D_{AB} \) is the enthalpy required to break the AB bond (the gas-phase A–B bond energy) and for the present discussion we employ individual, two-center bond indices. The bond indices satisfy the unity bond index condition:

\[ \sum_i (x_{Ai} + x_{Bi}) + x_{AB} = 1. \]  

In order to determine the binding energy we need to minimize the above energy expression subject to the constraint of Eq. (B.3). The Lagrangian energy function to optimize is

\[ L = E - \alpha \left[ \sum_i (x_{Ai} + x_{Bi}) + x_{AB} - 1 \right]. \] 

In the UBI–QEP method we optimize the energy directly in bond index space without knowledge of the specific geometry. Our definition of bond index requires, for example, that \( x_{AB} \) is unity at the equilibrium AB bond distance. Therefore we know the bond index at the energy minimum without knowing the bond distance.

Here we discuss the conditions under which the bond index space optimization gives the identical energy minimum as does coordinate space optimization. Remember that, in conventional methods, it is usual to compute the cartesian forces on the nuclei as the negative of the energy gradient with respect to the nuclear positions and adjust the positions of the atoms until the atomic forces fall below a certain threshold in magnitude. Let us define two sets of quantities, \( \{x_i\} \) is the set of bond indices, group or individual, for the active bonds, and \( \{q_i\} \) is a set of spatial coordinates in terms of which the forces on the atoms could be expressed. The set \( \{q_i\} \) could be cartesian coordinates of the atoms of the adsorbate or the distances between the atoms of the adsorbate and the metal atoms of the binding site or some other spatial coordinate system. With the help of the chain rule the forces in the spatial coordinate system can be expressed in terms of the bond index space forces as

\[ f_{q_i} = -\frac{\partial L}{\partial q_i} = -\sum_j \left( \frac{\partial L}{\partial x_j} \right) \frac{d x_j}{d q_i}, \]

where the summation runs over all the bond indices. If the UBI–QEP energy expression can be written so that the \( q_i \) coordinate contributes to one and only one bond index, then the vanishing of the forces at the equilibrium geometry, \( f_{q_i} = 0 \), necessarily requires that \( \partial L / \partial x_i \) vanish also, and therefore, the bond index space optimization results in the same energy minimum as coordinate space optimization. We refer to this as the rule of ‘one bond index for one spatial coordinate’ or the rule of ‘one-for-one’. The symmetry of the binding site, the unity bond index condition and sometimes group bond indices are employed to satisfy this rule of one-for-one. For example, in a diatomic, AB, the z (perpendicular) coordinate of atom A contributes to all the \( x_{Ai} \) as well as the \( x_{AB} \) bond indices. The unity bond index condition, Eq. (B.3), allows one to eliminate the \( x_{AB} \) bond index from the energy expression, and the symmetry of the binding site often allows one to reduce the number of \( x_{Ai} \) and \( x_{Bi} \) to one each.
For atomic binding on a unimetal surface, the UBI–QEP bond index space equations predict the binding sites to have $n$-fold symmetry. In the hollow site of the fcc(111) surface the three distances between the adatom, A, and the three metal atoms of the three-fold hollow compose a complete and non-redundant set of coordinates in which the motion of the A atom can be described. In this case the set of three distances, $r_i$, constitute a set of coordinates equivalent to the set of three cartesian coordinates of atom A, and the bond index space optimization of the UBI–QEP energy expression is entirely equivalent to a cartesian space optimization. In the two-fold bridge site and the ontop site both the bond index optimization and the coordinate space optimization require additional constraints to keep the atom in sites that are not energy minima in all possible directions of motion, but the rule of one-for-one is satisfied for these binding sites as well. Since the position of an atom is fixed in space by three coordinates, the set of four distances between the adatom and the four metal atoms comprising the four-fold hollow of the fcc(100) surface constitute a redundant coordinate system, and in principle, the corresponding four bond indices also form a redundant ‘coordinate system’ in which to express atomic forces. Geometry optimization in redundant coordinate systems has been discussed by Pulay et al. [254]. On bimetallic surfaces the hollow site atomic chemisorption has partial symmetry but not full symmetry and therefore the rule of one-for-one cannot always be strictly satisfied. However, the energy difference between the two energy minima is small.

In summary, the existence of a closed form solution for binding energies obtained from bond index space optimization that corresponds to the energy minimum obtained from geometry space optimization is tantamount to being able to write the UBI–QEP energy expression in such a way that the rule of one-for-one is satisfied or closely approximated. In the case of diatomic adsorbates on unimets, the optimization in bond index space is often equivalent to optimization in spatial coordinates. Some, but not all, of the bimetallic cases involve an additional approximation because the rule of one bond index per spatial coordinate is not always satisfied.

Appendix C. Heats of adsorption on bimetallic surfaces

In this appendix we consider the calculation of heats of adsorption on bimetallic surfaces. The UBI–QEP method does not make projections about the structure of the surface or the arrangement of the different types of metal atoms on the surface. Rather, the method begins with an arrangement of atoms and makes projections regarding the heats of adsorption and activation barriers given this specific arrangement of surface metal atoms. To test if the arrangement of surface atoms might be responsible for important effects, it is relatively easy to test all arrangements particularly when the method is automated as in a computer program.

C.1. Atomic chemisorption

By analogy with a unimetallic $M_n$-$A$ adsorption, the interaction potential between an adatom, $A$ and a bimetallic surface binding site, $M_iM_j$-$A$ (Fig. 14), is described by the sum of the two-body interactions:

$$E = \sum_{i=1}^{l} Q_{0A}(x_{i1}^2 - 2x_{i1}) + \sum_{j=1}^{l} Q_{0A}(x_{j2}^2 - 2x_{j2}).$$  \hspace{1cm} (C.1)
Here, the subscripts 1 and 2 of the bond indices correspond to bond indices involving metal atoms of type 1 and 2, respectively, and the primed quantities refer to the second type of metal atom. Firstly, we prove that, at equilibrium, the bond indices, $x_{ij}$, $i = 1, l$, are equal to each other and the bond indices, $x_{j2}$, $j = 1, l'$, are equal to each other. In other words, the bimetallic binding site will have symmetry but lower symmetry than the unimetallic case.

The Lagrangian for the constrained optimization is

$$L = E - \alpha \left( \sum_{i=1}^{l} x_{i1} + \sum_{j=1}^{l'} x_{j2} - 1 \right),$$

where $\alpha$ is the Lagrangian multiplier and the coefficient of $\alpha$ is the unity bond index constraint. Requiring that at the chemisorption minimum $\partial L/\partial x_{kl} = 0$, where $k = 1, l$, gives

$$x_{kl} = (\alpha + 2Q_{0A})/2Q_{0A}.$$  \hspace{1cm} (C.3)

Since there is no dependence on $k$ on the right-hand-side of Eq. (C.3), all $x_{kl}, k = 1, l$, have the same value at equilibrium. We simplify the subsequent development by adopting this symmetry at this point and write down a symmetric energy expression

$$E = lQ_{0A}(x_1^2 - 2x_1) + l'Q_{0A}'(x_2^2 - 2x_2).$$  \hspace{1cm} (C.4)

We have dropped the subscript, $i$, on $x_1$ (and similarly for $x_2$), since we have shown that they are all the same. The UBI condition is

$$lx_1 + l'x_2 = 1.$$  \hspace{1cm} (C.5)

Rather than employing the Lagrangian multiplier method, we enforce the constraint by directly substituting Eq. (C.5) into Eq. (C.4). Putting the $\partial E/\partial x_1 = 0$ gives for the equilibrium value of $x_1$:

$$x_1 = [l'Q_{0A} + Q_{0A}'(1 - l')]/(l'Q_{0A} + lQ_{0A}).$$  \hspace{1cm} (C.6)

When $Q_{0A} = Q_{0A}'$, the unimetallic result of $x_1 = 1/(l + l')$ is obtained.

Substitution of (C.6), and (C.5) into (C.4) gives for the heat of adsorption:

$$Q_A = [l'Q_{0A} + (1 - l')Q_{0A}']/l'(l'Q_{0A} + lQ_{0A}) + Q_{0A}'(2 - 1/l').$$  \hspace{1cm} (C.7)
Fig. 15. Admolecule AB erect in the three-atom binding site of a bimetallic surface with A as the contact atom. The binding site shown is composed of two metal atoms of type 1 (shaded circles), $l = 2$, and one metal atom of type 2 (open circles), $l' = 1$.

In the case that $Q_{0A} = Q_{0A}'$, Eq. (C.7) reduces to $Q_A = Q_{0A}(2 - 1/(l + l'))$ which is the unimetal result as it should be.

C.2. Mono-coordination

Some of the bimetallic chemisorption cases are quite simple due to their correspondence with unimetallic chemisorption. For example, the case of strong binding of an erect adsorbate, AB, with A being the contact atom, is directly analogous to the unimetal case in that Eq. (4.2.2.4) is used in both cases. The difference for chemisorption on a bimetallic surface is that the bimetallic atomic heat of adsorption, $Q_A$, from Eq. (C.7) is used for chemisorption on bimetallic surfaces.

The case of weak binding, described below, is more complex and is perhaps best evaluated with the aid of a computer program. The situation we consider immediately below is the weak and erect chemisorption of an adsorbate, AB with atom A being the contact atom, on a bimetallic surface. The mathematical problem is to minimize the UBI–QEP energy expression with respect to the bond indices under the unity bond index condition. We accomplish this employing the method of Lagrangian multipliers.

The binding site consists of $l$ metal atoms of type 1 and $l'$ metal atoms of type 2 (see Fig. 15). The UBI–QEP energy expression is

$$E = \sum_{i=1,l} Q_{0A}(x_{Ai}^2 - 2x_{Ai}) + \sum_{j=1,l'} Q_{0A}'(x_{Aj}^2 - 2x_{Aj}) + D_{AB}(x_{AB}^2 - 2x_{AB})$$

where primed quantities refer to the second type of metal. For simple diatomics, AB, the binding site has symmetry such that the $l$ bond indices, $x_{A1}, x_{A2}$, etc. are all equal to each other and we define the bond index $x_1$ to be this value. Similarly, the $l'$ bond indices are all the same and equal to $x_2$. For polyatomics, when B represents an atom group, this symmetry may be approximate, but presuming that atom A bonds to the center of the binding site in this case causes no significant errors. It is important to keep in mind that $x_1$ and $x_2$ are not group bond indices. The energy expression becomes

$$E = lQ_{0A}(x_1^2 - 2x_1) + l'Q_{0A}'(x_2^2 - 2x_2) + D_{AB}(x_{AB}^2 - 2x_{AB})$$

where $l$ and $l'$ are the number of type 1 and type 2 metal atoms, respectively.
This energy expression gives the energy of the system as a function of the bond indices up to dissociation along a line perpendicular to the surface that maintains the symmetry of the binding site at equilibrium. The unity bond index condition is

\[ l_x + l_x^t + x_{AB} = 1. \]  

(C.10)

The Lagrangian function to minimize is then

\[ L = E - \alpha(l_x + l_x^t + x_{AB} - 1). \]  

(C.11)

Putting the derivatives, \( \partial L/\partial x_1, \partial L/\partial x_2, \partial L/\partial x_{AB} \) and \( \partial L/\partial \alpha \) equal to zero gives the following matrix equation:

\[ A Y = \phi, \]  

(C.12)

where the skew-symmetric matrix is:

\[ A = \begin{pmatrix} 2lQ_{0A} & 0 & 0 & -l \\ 0 & 2l'Q_{0A} & 0 & -l' \\ 0 & 0 & 2D_{AB} & -1 \\ l & l' & 1 & 0 \end{pmatrix}, \]  

(C.13)

\( Y \) is a column vector having four elements: \( x_1, x_2, x_{AB} \) and \( \alpha \), and \( \phi \) is a column vector having four elements: \( 2lQ_{0A}, 2l'Q_{0A}, 2D_{AB} \) and 1. The vector, \( Y \), is the solution of Eq. (C.12) and is obtained by multiplying on the left by the left-hand inverse, \( B \), of the \( A \) matrix (\( BA = I \)). It is convenient to define another vector, \( C \), with elements \( l, l', 1, 1 \). Our convention is to use capital letters to represent matrices and vectors, bold-faced letters for matrices, and lower case letters to represent the elements of a matrix or vector. The elements of the \( B \) matrix are obtained by inverting the \( A \) matrix analytically:

\[ b_{i4} = (c_i/a_{ii})/\left( \sum_{k=1,3} c_k^2/a_{kk} \right), \quad i = 1, 3, \]  

(C.14)

\[ b_{44} = 1/\left( \sum_{k=1,3} c_k^2/a_{kk} \right), \]  

\[ b_{ii} = (1 - c_i b_{i4})/a_{ii}, \quad i = 1, 3, \]  

(C.15)

\[ b_{ij} = -c_i b_{i4}/a_{jj}, \quad i = 1, 4, \quad j = 1, 3, \quad i \neq j. \]  

(C.16)

The \( Y \) vector is given by

\[ Y = B\phi. \]  

(C.17)

Recalling that the elements of the \( Y \) vector, \( y_1, y_2, y_3 \) and \( y_4 \), are the equilibrium values of \( x_1, x_2, x_{AB} \) and \( \alpha \), respectively, the binding energy, \( Q_{AB} \), is given as \(- (E_{\text{min}} + D_{AB})\) which in terms of the elements of the \( Y \) vector is

\[ Q_{AB} = lQ_{0A}(2y_1 - y_1^2) + l'Q_{0A}(2y_2 - y_2^2) + D_{AB}(2y_3 - y_3^2 - 1). \]  

(C.18)

For medium strength bonding one takes the arithmetic average of the values obtained from strong and weak bonding.
C.3. Di-coordination

The model for di-coordination on close-packed surfaces seems to be coordination across a bridge site where the metal atoms are of different types. As in the case of unimetallic chemisorption in this binding site and coordination mode, the effect of crowding must be taken into account. This effectively scales the two-body binding energies, and we proceed, in direct analogy with the unimetallic case, to determine the effective parameters (see Ref. [38] or Appendix F).

First we determine the zero coverage limit binding energy of a single adsorbate atom, A, to the bimetallic n-fold site \( n = 2 \). This is given by Eq. (C.7) and we refer to this quantity as \( Q_{nA} \) or \( Q_{nB} \) depending on the adatom. Next, we determine the binding energy, \( Q_M \), of the metal atoms to the AB arrangement of adatoms, and A and B are treated as though they do not interact with each other. This is given by Eq. (4.8.3) with \( n = 2, m = 1 \) and \( m' = 1 \); \( Q_M(1,1) \). It is important to realize that the use of the bimetallic \( Q_{nA} \) and \( Q_{nB} \) in the expression for \( Q_M(1,1) \) creates an effective identity for the metal atoms. There is no different \( Q_M(1,1) \) for each type of metal. The alloy metal is now treated like a pure metal that is composed of a pseudo-type of metal atom that is an average of the metal types comprising the alloy. The individual metal–adatom binding strengths are differences of the form: \( Q_M(1,1) - Q_M(0,1) \). Then the coverage adapted binding energy of a single adatom A or B, \( Q^A(\theta) \) or \( Q^B(\theta) \), in the bridge site, \( n = 2 \), is constructed as the sum of the individual binding strengths with each pseudo-type metal atom. Since there are \( n = 2 \) pseudo-type metal atoms and both are involved in multi-adsorbate bonding, \( k = n = 2 \), the binding energies are:

\[
Q^A(\theta) = 2[Q_M(1,1) - Q_M(0,1)], \quad Q^B(\theta) = 2[Q_M(1,1) - Q_M(1,0)].
\]

The binding energy, \( Q_{AB} \), for horizontal chemisorption of the molecule, AB, on the bimetallic surface (Fig. 16) can then be obtained from Eqs. (C.9)–(C.18) with \( l = l' = 1 \), and \( Q^A(\theta) \) and \( Q^B(\theta) \) replacing \( Q^{0A} \) and \( Q'^{0A} \), respectively.

For the case of chelating adsorbates on bimetallic surfaces, Eq. (4.3.2.3.1) is used and the \( Q_{AX} \) is interpreted to be heat of adsorption of the AX fragment on the bimetallic surface.

The development of the binding energy in the case of asymmetric coordination of an adsorbate ABC in the bridging site of bimetallic surfaces (Fig. 17) parallels that of the unimetallic case.

The quasi-atom heat of adsorption for the BC fragment is obtained for each pure metal as described in the case of unimetallic chemisorption giving \( Q^{0(BC)} \) and \( Q'^{0(BC)} \). The binding energy of the BC

![Fig. 16. Admolecule AB in a bridge site of a bimetallic surface. The shaded circles correspond to metal atoms of type 1. and the open circles indicate metal atoms of type 2.](image-url)
pseudo-atom, $Q_{n\{BC\}}$, on the alloy surface is obtained from Eq. (C.7) employing $Q_{0\{BC\}}$ and $Q'_{0\{BC\}}$. The coverage dependent binding energy, $Q_{2\{BC\}}(\theta)$, is then obtained from Eq. (C.19) which makes use of Eq. (4.8.3). The $Q_{2A}(\theta)$ parameter is defined in Eq. (C.19) and the binding energy of the quasi-diatomic, A–BC, in the bridging site of the alloy is obtained from Eqs. (C.9)–(C.18) with $l = l' = 1$, and $Q_{2A}(\theta)$ and $Q_{2\{BC\}}(\theta)$ replacing $Q_{0A}$ and $Q'_{0A}$, respectively.

**Appendix D. Properties of the transition state for a dissociating (pseudo-) diatomic molecule**

The UBI-QEP method allows the projection of intrinsic activation barriers which implies a specific energy for the transition state, which in turn implies values for the bond indices in the transition state. In this section we develop the system of equations that give these implied bond indices for the transition state. An equivalent development is given in Ref. [39] (cf. p. 109, Eq. (21b)). We begin with an energy expression and the UBI constraint for the dissociating AB molecule:

$$E = Q_A(x_A^2 - 2x_A) + Q_B(x_B^2 - 2x_B) + D_{AB}(x_{AB}^2 - 2x_{AB}), \quad (D.1)$$

$$x_A + x_B + x_{AB} = 1, \quad (D.2)$$

where the bond indices, $x_A$ and $x_B$, may be group or individual bond indices. $Q_A$ and $Q_B$ are the interaction energies between the A and B fragments and the surface under the prevailing conditions.

The solution to the problem under consideration is in hand when the energy, Eq. (D.1), is the energy of the transition state, given by the interpolation technique of Section 4.6, so that $x_{AB} = x_{AB,TS}$. The transition state is a saddle point on the minimum energy reaction path. Therefore the energy is a minimum with respect to $x_A$ and $x_B$ subject to the UBI constrain, Eq. (D.2), at every point along the minimum energy reaction path, which includes the transition state. We use the method of Lagrangian multipliers to conduct the constrained optimization of the energy which gives us expressions for $x_A$ and $x_B$ in terms of $x_{AB}$ and the thermodynamic parameters. Then the energy is set equal to the energy of the transition state and $x_{AB}$ is determined, which in turn gives the values of $x_A$ and $x_B$ at the transition state.
The Lagrangian energy functional is

\[ L = E - \alpha(x_A + x_B + x_{AB} - 1). \]  

Putting the derivatives, \( \partial L / \partial x_A, \partial L / \partial x_B, \partial L / \partial \alpha \), to zero allows us to express \( x_A \) and \( x_B \) in terms of \( x_{AB} \). This gives the matrix equation

\[ AY = \phi, \]  

where the skew-symmetric \( A \) matrix is

\[ A = \begin{pmatrix} 2Q_A & 0 & -1 \\ 0 & 2Q_B & -1 \\ 1 & 1 & 0 \end{pmatrix}. \]  

\( Y \) is a column vector having three elements: \( x_A, x_B, \) and \( \alpha \), and \( \phi \) is a column vector having three elements: \( 2Q_A, 2Q_B, \) and \( 1 - x_{AB} \). The vector, \( Y \), is the solution of Eq. (D.4) and is obtained by multiplying on the left by the left-hand inverse, \( B \), of the \( A \) matrix (\( BA = I \)). The elements of the \( B \) matrix are:

- row 1: \( b_{11} = (1 - b_{13})/2Q_A; \) \( b_{12} = -b_{13}/2Q_B; \) \( b_{13} = 2Q_A/(Q_A + Q_B); \)
- row 2: \( b_{21} = (1 - b_{23})/2Q_A; \) \( b_{22} = (1 - b_{23})/2Q_B; \)
- row 3: \( b_{31} = (1 - b_{33})/2Q_A; \) \( b_{32} = (1 - b_{33})/2Q_B; \) \( b_{33} = 2Q_AQ_B/(Q_A + Q_B) \).

The values of \( x_A \) and \( x_B \) are obtained as a function of \( x_{AB} \) by multiplying Eq. (D.4) on the left by \( B \): \n
\[ x_A = 2Q_Ab_{11} + 2Q_Bb_{12} + b_{13}(1 - x_{AB}) = 1 - Q_B(x_{AB} + 1)/(Q_A + Q_B), \]  

\[ x_B = 2Q_Ab_{21} + 2Q_Bb_{22} + b_{23}(1 - x_{AB}) = 1 - Q_A(x_{AB} + 1)/(Q_A + Q_B). \]  

Substitution of Eqs. (D.6) into Eq. (D.1) gives the energy along the minimum energy reaction path in terms of \( x_{AB} \). Therefore, when the energy equals the energy of the transition state, \( x_{AB} \) is the \( A-B \) bond index of the transition state. The energy of the transition state relative to surface adsorbed reactant is

\[ E_{TS} = E_{\text{min}} + \Delta E_{AB}^*, \]  

where \( E_{\text{min}} \) is the energy minimum of the chemisorbed \( AB \) molecule and \( \Delta E_{AB}^* \) is the activation barrier for the forward reaction given in Section 4.6. Since the zero point in the energy function occurs when all bond indices are zero, i.e. \( AB \) desorbed and dissociated into \( A \) and \( B \), the energy minimum is given by

\[ E_{\text{min}} = -D_{AB} - Q_{AB}, \]  

where \( D_{AB} \) is the \( AB \) bond enthalpy and \( Q_{AB} \) is the heat of adsorption of \( AB \). Putting Eq. (D.1) equal to Eq. (D.7) using Eqs. (D.6) gives a quadratic expression for the value of \( x_{AB,TS} \):

\[ C_2x_{AB,TS}^2 + C_1x_{AB,TS} + C_0 = 0, \]  

and

\[ C_2 = Q_AQ_B/(Q_A + Q_B) + D_{AB}, \quad C_1 = 2Q_AQ_B/(Q_A + Q_B) - 2D_{AB}, \]  

\[ C_0 = Q_AQ_B/(Q_A + Q_B) - Q_A - Q_B - E_{TS}. \]  

Since Eq. (D.9) is quadratic, two solutions are obtained for any given value of ETS. However, it is usually clear that one of the two values is the physically less reasonable of the two. For example, often
one of the solutions to Eq. (D.9) will either be outside the legitimate range of 0 ≤ x ≤ 1 or will give an illegitimate value for xA or xB from Eqs. (D.6). Also, if a value for xAB.TS is larger than the chemisorbed equilibrium AB bond index, then it should be rejected.

At first sight, one might ask why do we not simply maximize the Lagrangian energy functional, Eq. (D.3), employing Eq. (D.6) as a way to determine the transition state AB bond index. The answer is that there is no maximum in this functional with respect to xAB. The UBI condition that we impose is not valid beyond the transition state because the dissociated fragments should be independent of each other and not linked through the UBI condition.

Appendix E. Diffusion effects

In this section we consider the development of the diffusion contribution to apparent reaction rate constants and activation barriers for recombination and disproportionation reactions A1 + B1 → Product. The products are ABs and Ys + Zs for recombination and disproportionation, respectively. We first discuss atomic diffusion followed by the mechanism of recombination and disproportionation.

The atomic heat of adsorption is related to the diffusion activation barrier through the corrugation ratio

\[ \gamma_n = \frac{\Delta E_{\text{diff},A}^*}{Q_{nA}}. \]  

(E.1)

The diffusion of atoms is assumed to proceed via a hopping mechanism along the minimum energy migration path [131]; n-fold hollow → bridge site → n-fold hollow so that the diffusion barrier is

\[ \Delta E_{\text{diff},A}^* = Q_{nA} - Q_{2A}. \]  

(E.2)

The UBI–QEP method yields for the corrugation ratio [131]

\[ \gamma_n = 1 - Q_{2A}/Q_{nA} = (n-2)/(4n-2), \quad n > 2, \]  

(E.3)

so that the expression for the diffusion activation barrier for atoms is

\[ \Delta E_{\text{diff},A}^* = \gamma_n Q_{nA} = Q_{nA} (n-2)/(4n-2), \]  

(E.4)

where \( n = 3, 4, 5 \) for fcc(1 1 1), fcc(1 0 0) and bcc(1 0 0) surfaces, respectively.

The mechanism of recombination and disproportionation reactions which we adopt here is a two-stage mechanism. The first step is an equilibrium between the reactants and a precursor state which is composed of reactants that are in a close enough proximity for the reaction to occur. The second step is the formation of the product from the precursor state

\[ A + B \leftrightarrow A^+ + B^+ \rightarrow \text{Product}. \]  

(E.5)

In this mechanism the rate of formation of the precursor state, \( A^+ + B^+ \), from the reactants is

\[ \text{rate}_1 = D[A][B], \]  

(E.6)

where \( D \) is the mutual diffusivity of the reactants, and, the quantities in square brackets are the surface densities of the corresponding adsorbate. The rate of the reverse of this reaction is

\[ \text{rate}_{-1} = D[A^+ + B^+], \]  

(E.7)
where $D^\dagger$ is the diffusivity of the precursor state (analogous to a transition state) and $[A^\ddagger + B^\ddagger]$ is the surface density of adsorbates in the precursor state. The rate of product formation is

$$\text{rate}_2 = \frac{d[\text{Product}]}{dt} = k_{\text{int}}[A^\ddagger + B^\ddagger]$$  \hspace{1cm} (E.8)

and $k_{\text{int}}$ is the intrinsic rate constant. We obtain an expression for $[A^\ddagger + B^\ddagger]$ in terms of the other parameters by applying the steady state approximation to $[A^\ddagger + B^\ddagger]$. The time derivative of the precursor state density, $[A^\ddagger + B^\ddagger]$, is zero which means that $\text{rate}_1 - \text{rate}_2 = 0$, from which we obtain

$$[A^\ddagger + B^\ddagger] = \frac{D[A][B]}{(D^\dagger + k_{\text{int}})}.$$  \hspace{1cm} (E.9)

Substituting this into Eq. (E.8) gives

$$\text{rate}_2 = \frac{d[\text{Product}]}{dt} = k_{\text{int}}D[A][B]/(D^\dagger + k_{\text{int}}).$$  \hspace{1cm} (E.10)

so that the apparent rate constant is

$$k_{\text{app}} = \frac{k_{\text{int}}D}{(D^\dagger + k_{\text{int}})}.$$  \hspace{1cm} (E.11)

The activation barrier for a process is related to the corresponding rate constant by assuming the Arrhenius forms:

$$k = A \exp\left\{ -\frac{\Delta E^*}{k_B T} \right\}$$  \hspace{1cm} (E.12)

and

$$D = D_0 \exp\left\{ -\frac{\Delta E^*_{\text{dif}}}{k_B T} \right\}.$$  \hspace{1cm} (E.13)

where $A$ and $D_0$ are the Arrhenius pre-exponential factors, $\Delta E^*$ is the activation barrier, $\Delta E^*_{\text{dif}}$ is the diffusion barrier, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. We take as the definition of the apparent activation barrier

$$\Delta E_{\text{app}}^* = -k_B [d \ln(k_{\text{app}})/d(1/T)].$$  \hspace{1cm} (E.14)

The mutual diffusion barrier of $A + B$, $\Delta E^*_{\text{dif},A+B}$, and that of the precursor state, $A^\ddagger + B^\ddagger$, $\Delta E^*_{\text{dif},A^\ddagger+B^\ddagger}$, are the same, neglecting local coverage effects, since the only difference between the two situations is that the adsorbates in the precursor state are closer together. Substitution of (E.11) into (E.14) gives an expression for the apparent activation barrier:

$$\Delta E_{\text{app}}^* = \alpha \Delta E_{\text{int}}^* + (1 - \alpha) \Delta E^*_{\text{dif},A^\ddagger+B^\ddagger},$$  \hspace{1cm} (E.15)

where

$$\alpha = \frac{D^\dagger}{(D^\dagger + k_{\text{int}})}.$$  \hspace{1cm} (E.16)

Since $\alpha$ has a range between 0 and 1, it is clear that $\Delta E_{\text{app}}^*$ is bounded by $\Delta E_{\text{int}}^*$ and $\Delta E_{\text{dif},A^\ddagger+B^\ddagger}$. The fact that $\alpha$ is dependent on temperature does not negate this fact. In other words, Eq. (E.15) has the form of a linear interpolation in the variable $\alpha$. When the mutual diffusion barrier is large compared to the intrinsic activation barrier, then $\alpha \approx 0$ and the apparent activation barrier is well approximated by the mutual diffusion barrier. Conversely, when the intrinsic activation barrier is large enough compared to the diffusion barrier so that $D^\dagger \gg k_{\text{int}}$, then $\alpha \approx 1$ and the apparent activation barrier is approximated by the intrinsic activation barrier. In both cases the apparent activation barrier is approximated by the larger of the two component barriers when one is large compared to the other.
We need now an estimate of the diffusion barrier for the mutual diffusion of A and B, \( \Delta E_{\text{diff}, A+B}^* \). Recalling that [131]:

\[
D_{A+B} = D_A + D_B, \tag{E.17}
\]

the derivative of \( D_{A+B} \), (E.13), with respect to reciprocal temperature gives for \( \Delta E_{\text{diff}, A+B}^* \):

\[
\Delta E_{\text{diff}, A+B}^* = \beta \Delta E_{\text{diff}, A}^* + (1 - \beta) \Delta E_{\text{diff}, B}^*, \tag{E.18}
\]

where

\[
\beta = D_A / (D_A + D_B). \tag{E.19}
\]

Since \( \beta \) varies from 0 to 1, it is clear that the value of \( \Delta E_{\text{diff}, A+B}^* \) is bounded by \( \Delta E_{\text{diff}, A}^* \) and \( \Delta E_{\text{diff}, B}^* \). When \( \Delta E_{\text{diff}, B}^* \gg \Delta E_{\text{diff}, A}^* \), then \( D_A \gg D_B \) so that \( \beta \approx 1 \) and \( \Delta E_{\text{diff}, A+B}^* \approx \Delta E_{\text{diff}, A}^* \). So, in the case that one surface reactant is immobile, the mutual diffusion barrier, \( \Delta E_{\text{diff}, A+B}^* \), is well approximated as the lesser of the two component barriers. Again, Eq. (E.18) has the form of a linear interpolation in the variable \( \beta \). Therefore, to estimate the value of \( \Delta E_{\text{diff}, A+B}^* \) one may interpolate between the two extremes. For example, we can employ the harmonic average:

\[
\Delta E_{\text{diff}, A+B}^* \approx \frac{2 \Delta E_{\text{diff}, A}^* \Delta E_{\text{diff}, B}^*}{\Delta E_{\text{diff}, A}^* + \Delta E_{\text{diff}, B}^*}, \tag{E.20}
\]

which is superior when one barrier is significantly greater than the other:

\[
\Delta E_{\text{diff}, A}^* \ll \Delta E_{\text{diff}, B}^*. \tag{E.21}
\]

Then the mutual diffusion barrier is

\[
\Delta E_{\text{diff}, A+B}^* \approx 2 \Delta E_{\text{diff}, A}^*. \tag{E.22}
\]

Now that we can estimate the values of \( \Delta E_{\text{diff}, A}^* \), \( \Delta E_{\text{diff}, B}^* \) and \( \Delta E_{\text{diff}, A+B}^* \), we can estimate the relative importance of diffusion in the apparent activation barriers (see Section 4.7).

**Appendix F. Accounting for coverage effects**

In accounting for coverage effects we first consider the strength of the two-center interactions for the case of an atom in an \( n \)-fold surface site: \( M_n - A \). The atomic binding energy in this \( n \)-fold site is:

\[
Q_{nA} = Q_{0A}(2 - 1/n). \tag{F.1}
\]

Since each of the \( n \) two-center interactions is equivalent to the others, we assign a strength to each of them of \( Q_{nA}/n \). Now we consider that a metal atom of this \( n \)-fold site interacts with \( m \) adatoms: \( M - A_m \). This binding situation has \( m \)-fold symmetry so that the UBI-QEP energy expression for this arrangement of atoms is

\[
E = m(Q_{nA}/n)(x_M^2 - 2x_M) \tag{F.1}
\]

and the unity bond index condition is

\[
x_M = 1. \tag{F.2}
\]

Substitution of Eq. (F.2) into (F.1) gives for the binding energy of \( M \) to this arrangement of adatoms, \( A_m \):

\[
Q_M = -E = (Q_{nA}/n)(2 - 1/m). \tag{F.3}
\]
Each of the \( m \) two-center interactions of the \( M-A_m \) complex has a strength of
\[
Q_M/m = (Q_{nA}/mn)(2 - 1/m).
\] (F.4)

The metal atoms of the \( n \)-fold site might bind to differing numbers of adatoms, and therefore, they may each have a different \( m \) value, \( m_i \). The metal atoms of the \( n \)-fold site having the same \( m \) value, \( m_i \), belong to the same ‘local-symmetry’ type, and \( k_i \) is the number of metal atoms of the \( n \)-fold site of the \( i \)th local-symmetry type.

The new atomic heat of adsorption in the presence of coadsorbates is constructed by summing the two-center contributions. The following formula is obtained by replacing \( m \) in Eq. (F.4) with \( m_i \), multiplying \( (Q_M/m_i) \) by \( k_i \) to account for the number of metal atoms of the \( i \)th type, and summing over the local-symmetry types:
\[
Q_{nA}(\theta) = Q_{nA}(1/n) \sum_i (k_i/m_i)(2 - 1/m_i).
\] (F.5)

Therefore the scale factor that converts the zero coverage limit heat of adsorption into the coverage dependent value is
\[
\sigma = Q_{nA}(\theta)/Q_{nA} = (1/n) \sum_i (k_i/m_i)(2 - 1/m_i).
\] (F.6)

In the case that the coadsorbate of adatom A is an adatom of a different type, B, the development is slightly more complex. The strength of the two-center interactions for the case of an atom in an \( n \)-fold surface site: \( M_n-A \) or \( M_n-B \) is \( Q_{nA}/n \) and \( Q_{nB}/n = Q_{0Y}(2 - 1/n)/n \), where \( Y \) can be A or B. A metal atom of this \( n \)-fold site interacts with \( m \) atoms of type A and \( m' \) atoms of type B: \( M-A_mB_{m'} \). The binding energy of the single metal atom to the cluster of adatoms is obtained from the minimization of the UBI–QEP energy expression
\[
E = (Q_{nA}/n)(x_A^2 - 2x_A) + (Q_{nB}/n')(x_B^2 - 2x_B),
\] (F.7)
subject to the unity bond index condition
\[
mXA + m'XB = 1,
\] (F.8)
which includes the presumption that lateral interactions between the adatoms can be neglected. Substitution of (F.8) into (F.7) followed by putting \( \partial E/\partial x_A = 0 \) gives the value of \( x_A \) at the chemisorbed equilibrium as
\[
x_A = [m'(Q_{nA} - Q_{nB}) + Q_{nB}]/(m'Q_{nA} + mQ_{nB}).
\] (F.9)

Eq. (F.9) reduces to the corresponding expressions in the literature for the case of \( m = m' = 1 \) [38], and the equilibrium value of \( x_B \) is fixed by Eq. (F.8). The homoatomic result is obtained by putting \( Q_{nA} = Q_{nB} \) and \( x_A \) reduces to \( 1/(m + m') \) as is the required result when B and A atoms are identical. Substitution of Eq. (F.9) into (F.7) gives the binding energy of the metal atom to \( A_mB_{m'} \):
\[
Q_M(m, m') = -E = Q_{nB}(2 - 1/m')/n + mq^2/m'nd,
\] (F.10)
where
\[
q = m'(Q_{nA} - Q_{nB}) + Q_{nB}
\] (F.11)
and
\[
d = m'Q_{nA} + mQ_{nB}.
\] (F.12)
Putting $Q_{nB} = Q_{nA}$ in Eqs. (F.10)–(F.12) gives $Q_M(m, m') = Q_{nA}(2 - 1/(m + m'))/n$ which is the correct homoatomic result. It is also required that $Q_M(m, m')$ does not change with increasing $m$ if $Q_{nA}$ is zero. It is straightforward to show that $\partial Q_M(m, m')/\partial l = 0$ in the limit that $Q_{nA}$ goes to zero. This binding situation has such symmetry that the $m$ M–A interactions are equivalent and the $m'$ M–B interactions are equivalent. Therefore the strength of the individual metal–adatom interactions is:

$$Q_{0A}(\theta) = (Q_M(m, m') - Q_M(0, m'))/m,$$
$$Q_{0A}(\theta) = q^2/(m'nd)$$

and relabeling the atoms gives for adatoms of type B:

$$Q_{0B}(\theta) = (Q_M(m, m') - Q_M(m, 0))/m',$$
$$Q_{0B}(\theta) = q^2/(mnd) \text{ with } q \text{ properly relabeled.}$$

The $Q_M(0, m')$ and $Q_M(m, 0)$ correspond to the case of homoatomic adatoms and are equal to $Q_{nB}(2 - 1/m')/n$ and $Q_{nA}(2 - 1/m)/n$, respectively. The new atomic heat of adsorption in the presence of coadsorbates is constructed by summing the two-center bond strengths, and several examples of this are given in Section 4.8.

**Appendix G. A modified UBI–QEP potential function for molecular dynamics simulations of reactions on metal surfaces**

In our adaptation of the UBI–QEP method to the simulation of reactions on metal surfaces, the sum of the bond indices is *normalized* rather than conserved in order that the normalization condition describes both the reactant state as well as the product state [133–135]. Therefore we use a slightly different acronym (normalized bond index or NBI) for the method. The bond index normalization is applied to the minimum energy hypersurface. Motion off the minimum-energy surface is not directly influenced by the normalization. The normalization condition is

$$\beta(Z_A + Z_B) + x_{AB} = N \quad \text{and} \quad N = 1 + (2\beta - 1)\exp\{-\gamma \Delta^i\}, \quad (G.1)$$

where $x_{AB}$ is the usual AB bond index, and $Z_A$ and $Z_B$ are *interaction indices*. The normalization condition, (G.1), can be generalized to include more than one active adsorbate bond. No mapping of geometry parameters onto $Z_A$ or $Z_B$ is imposed and we allow them to take on negative values to describe repulsions with the surface when $x_{AB}$ is greater than unity. The $\beta$ parameter is sometimes used to account for the locally high coverage situation when a weakly bound molecule binds horizontally in the bridge site. This is another way of accomplishing the same task as scaling the atomic heats of adsorption as was done in the UBI–QEP method to account for coverage effects. Both approaches result in lower bond/interaction indices in the molecular chemisorption state and have no effect in the dissociation limit. The $\beta$ parameter is adjusted until the heat of adsorption of the molecule agrees with either the UBI–QEP projection or a reliable experimental value. The value of this parameter can also be fixed [135] by requiring $\beta Z_A(\theta = 0) = Z_A(\theta)$ where $Z_A(\theta)$ is the surface-A bond index for local coverage $\theta$ for AB on the surface, e.g., AB in the bridge site. The $\gamma$ parameter of Eq. (G.1) is determined by fitting the Arrhenius activation barrier from molecular dynamics simulations in a suitable temperature range to either an accurate experimental value or the
UBI–QEP projected value. For reactions in which there are no barriers, we have seen that a value of $\gamma = 2$ works well.

The $\Delta$ function is defined as

$$\Delta = \frac{x_{AB}}{(1 - x_{AB})} \quad \text{for} \quad x_{AB} < 1.$$  

$\Delta$ is infinite for $x_{AB} \geq 1$. \hspace{1cm} (G.2)

That Eqs. (G.1) describe both product and reactant states is clear from examining the limiting behavior. When $x_{AB} \approx 1$, the normalization function, $N$, is unity. At the dissociation limit, $x_{AB} \approx 0$ and the normalization function is $2/3$ which allows both $Z_A$ and $Z_B$ to be unity (see below). The AB bond index is usually taken to be the single-term Pauling-type bond order

$$x_{AB} = \exp\left\{ - \frac{R_{AB} - R_{AB,eq}}{a_{AB}} \right\}, \hspace{1cm} (G.3)$$

where $R_{AB}$ and $R_{AB,eq}$ are the AB bond distance and equilibrium bond length, respectively. The Morse parameter, $a_{AB}$, is derived from the quadratic force constant, $F_k$, and the dissociation energy, $D_{AB}$:

$$a_{AB} = \left[ \frac{2D_{AB}}{F_k} \right]^{1/2}. \hspace{1cm} (G.4)$$

The potential energy function is defined by:

$$V = Q_A(Z_A^2 - 2Z_A) + Q_B(Z_B^2 - 2Z_B) + D_{AB}(x_{AB}^2 - 2x_{AB}),$$

$$Q_A = -q_A(W_A^2 - 2W_A) \quad \text{for} \quad Z_A \geq 0,$$

$$Q_A = q_A(W_A^2 - 2W_A) \quad \text{for} \quad Z_A < 0 \text{ and } W_A > 2;$$

$$q_A = \sum_i G_1 \exp(-\mu_1\rho_i^4) + \sum_i \rho_i^2 G_2 \exp(-\mu_2\rho_i^2). \hspace{1cm} (G.5)$$

$$W_A = \exp\left\{ - (R_A - R_{A,eq})/a_A \right\},$$

$$R_{A,eq} = R_0 - a_A \ln\{1/(2 - q/q_0)\}.$$  

The information about the topology of the surface is contained in the $q$ and $W$ functions, and the $Q_A$ are Morse potentials having as the variable the distance perpendicular to the surface. The variable, $\rho_i$, is the projection of the position vector relative to the $i$th metal atom of the adatom onto the plane of the surface, and the summation runs over these distances that are less than a prespecified cutoff. The parameters of the $q$ function, $G$ and $\mu$, are determined by fitting to the UBI–QEP atomic binding energies in the ontop, bridge and hollow sites. The $q$ function is certainly not unique and other functions that represent the atomic binding energy surface would serve as well. In our O$_2$ example in the text, we also required the energy points between the binding site energies to follow a regular curve such as a sine curve. The parameters of the $q$ function are determined by least squares fit to these data. The equilibrium distance above the surface, $R_{A,eq}$, is a function of the position above the surface as indicated above. $R_0$ and $q_0$ are respective quantities corresponding to the ontop site. The equation defining $R_{A,eq}$ derives from an equation given by Shustorovich [38] in which integer quantities have been generalized to continuous variables.

The interaction indices, $Z_A$ and $Z_B$, are determined by requiring that the minimum energy function ($W_A = W_B = 1$) be a minimum with respect to them under the normalization constraint. The variational procedure yields [135]:

$$Z_A = ((q_A - q_B) + q_B(N - x_{AB})/\beta)/(q_A + q_B),$$

$$Z_B = ((q_B - q_A) + q_A(N - x_{AB})/\beta)/(q_A + q_B). \hspace{1cm} (G.6)$$
At the dissociation limit (Eq. (G.1), \( x_{AB} = 0 \) and \( \beta(Z_A + Z_B) = N = 2/\beta \), so that \( Z_A + Z_B = 2 \). It is also seen from Eq. (G.6) with these limiting values that \( Z_A = Z_B = 1 \).

The potential function, Eqs. (G.5), allows the AB molecule to properly vibrate. This is seen at the desorption limit at which \( W_A \) and \( W_B \) are small or zero and the potential reduces to the Morse potential for the AB molecule. The influence of the bond index normalization automatically vanishes as the molecule desorbs (\( x_{AB} = 1 \)).

In the UBI–QEP method repulsive interactions are taken into account indirectly through the UBI constraint. Here, there are a couple of situations in which repulsions with the surface are generated. Firstly, when \( x_{AB} > 1 \) (\( R_{AB} < R_{AB,eq} \)) one or both of the interaction indices, \( Z_A \) and \( Z_B \), will be negative. The negative interaction index causes a repulsion to exist between that atom and the surface. We consider that this is physically reasonable. Secondly, when \( W_A \) or \( W_B \) is > 1 the corresponding atom is on the repulsive wall of the \( Q \) function. Thirdly, with \( R_{AB} > R_{AB,eq} \) so that \( x_{AB} < 1 \), Eqs. (G.6) allow situations in which one of the interaction indices, \( Z \), can be negative. In the present formulation, this generates a repulsion between that adatom and the surface. An example of this is a homonuclear diatomic molecule on an fcc(111) surface oriented with one atom in the hollow site with the other atom leaning toward an ontop site. The atom tending toward the ontop site will experience a weak repulsive interaction. A special case we have encountered is the case in which an adatom, say atom A, gets close to the surface so that \( Q_A \) becomes negative while simultaneously \( Z_A \) is negative. Without correcting for this double negative situation, an unintended net attraction results. When this condition occurs, one retains the desired repulsion by changing the sign of \( Q_A \). This causes no difficulty in the dynamics.

The potential function of Eqs. (G.5) with parameters for O on Ag(111) of \( \beta = \gamma = i = 2 \) describes well the major features of the reactive energy hypersurface. The heat of adsorption of \( O_2 \) in the bridging site agrees well with the experimental and UBI–QEP values; the bridge binding site represents a true molecular chemisorption minimum and the enthalpy of the surface reaction is correct. There may well be minor discrepancies between our phenomenological potential surface and the exact potential, however, our results indicate that minor features do not have important effects on the reaction rate.

References

[76] UBI-Model is a computer program developed in the research group of Harrell Sellers at South Dakota State University that performs UBI-QEP calculations of reaction energetics and NBI calculations of reaction rate constants.
[118] See, for example, Refs. [31-34] and discussions in Ref. [35] and references therein.
[121] P.M. Morse, Phys. Rev. 34 (1929) 57.
[124] (a) See, for example Ref. [37(g)]; (b) E. Shustovorovich, unpublished results.
[126] L. Dubois, private communication.


E. Shustorovich, H. Sellers, Surface Science Reports 31 (1998) 1-119