Local Isoelectronic Reactivity of Solid Surfaces

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The quantity $w^N(\mathbf{r}) = (1/k^2 T_{\text{el}})[\partial n(\mathbf{r}, T_{\text{el}})/\partial T_{\text{el}}]_{v(\mathbf{r}),N}$ is introduced as a convenient measure of the local isoelectronic reactivity of surfaces. It characterizes the local polarizability of the surface, and it can be calculated easily. The quantity $w^N(\mathbf{r})$ supplements the charge transfer reactivity measured, e.g., by the local softness to which it is closely related. We demonstrate the applicability and virtues of the function $w^N(\mathbf{r})$ for the example of hydrogen dissociation and adsorption on Pd(100). [S0031-9007(96)01022-8]

Density-functional calculations of chemisorption processes and of potential energy surfaces of the dissociation of simple molecules over surfaces, which have become available in the last few years, have greatly improved the fundamental understanding of reactions at solid surfaces. However, those extensive computations are limited to a restricted number of model systems. It remains an important task to develop a methodology that allows the prediction and interpretation of reactions at surfaces in terms of the properties of the noninteracting systems. Such concepts, well known in molecular chemistry, are the essence of "reactivity theory." They are based on low-order perturbation theory and aim at a description of the early stages of chemical interactions. The ensuing response functions are called "reactivity indices" and characterize the changes of the electronic structure of one reactant as stimulated by the presence of the other or vice versa. In an early contribution to this field, Fukui *et al.* [1,2] established the correlation between the frontier-orbital density, i.e., the density of the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO), and the reactivity of a system toward electron donation or acceptance. Pearson [3] introduced the electronic "softness," the magnitude of the change of the electronic structure due to a change of the number of electrons in the system, as a measure of the reactivity. Species are classified as "soft" if only a small energy is required to change their electronic configuration, i.e., if the valence electrons are easily distorted, polarized, removed or added. A "hard" species has the opposite properties, holding its valence electrons more tightly [3,4]. The utility of the hardness-softness concept is based on the so called hard and soft acid and base (HSAB) principle formulated by Pearson [3] which states that hard-hard (soft-soft) interactions are preferred. In the case of polyatomic or extended systems, the HSAB principle is used in a local version: The soft (hard) parts of one reactant prefer to interact with soft (hard) areas of the other [5]. Parr and collaborators [5] gave a foundation in density functional theory to those mostly semiempirical concepts, and Cohen *et al.* [6–8] have reviewed the foundations of reactivity theory and addressed some unresolved issues.

The (local) softness and hardness describe the response of the electron density to a change of the charge state of the system. For extended, gapless systems the local softness $s(\mathbf{r})$ is defined as

$$s(\mathbf{r}) = \left[\frac{\partial n(\mathbf{r})}{\partial \mu} \right]_{v(\mathbf{r}),T_{\text{el}}}, \qquad (1)$$

where $v(\mathbf{r})$ is the electrostatic potential due to the nuclei, and T_{el} is a temperature (see below). The global softness S is defined as the integral of the local softness over all space. The local softness is the local density of states at the Fermi energy, $g(\mathbf{r}, \mu)$, screened by a response function closely related to the static dielectric function [7]; it describes the *local* response of the electron density to a *global* change of the charge state of the system. The chemical interaction will be, however, largely determined by the *nonlocal* response of the electron density to a *local* perturbation, and is governed by the whole spectrum and not just the states at the Fermi energy [6]. Despite these restrictions, the local softness, in connection with the HSAB principle, has become an important predictive tool in analyzing reactions between molecules [9,10].

From the beginning, application of the softness concept to surface processes and, in particular, to catalytic reactions at metal surfaces has been proposed, and empirical rules, e.g., for the influence of adsorbate layers on the surface properties of metals, have been deduced [3,11–13]. However, for extended systems molecular orbitals and levels are not well defined and models of chemical reactions at surfaces are reformulated using a basis of localized atomlike orbitals and the projected density of states (see, e.g., [14–17]). Only recently investigations appeared which apply the HSAB principle to semiconductor systems [18–21]. Calculations of the local softness at metal surfaces have not yet been done so far. Metal surfaces are characterized by a nonzero density of states

(DOS) at the Fermi level, and screen external perturbations efficiently by low-energy electron-hole excitations. In the framework of reactivity theory, the metal surface is thus soft. In much the same spirit, Feibelman and Hamann [22] related the change of reactivity of transition metal surfaces in the presence of adsorbate layers to the spatial variation of the DOS at E_F. Although their study demonstrated that the states in the vicinity of the Fermi level govern the reactivity of metal surfaces, no clear correlation between local reactivity and the spatial variations of the DOS close to E_F could be established. Falicov and Somorjai [23] stressed the importance of low-energy occupation fluctuations for the large reactivity of metal surfaces. Yang and Parr [12], as well as Baekelandt *et al.* [24], have shown that the local softness is directly related to the correlation function of changes of the total number of electrons and the density fluctuations.

In this paper we introduce the change of the electron density due to the excitation of low-energy electron-hole pairs induced by an increased electron temperature, T_{el}, as a quantity which characterizes the spatial distribution of the reactivity of metal surfaces. We show that this isoelectronic reactivity index, denoted as $w^N(\mathbf{r})$, represents a convenient measure of the capability of the metal electrons to react in response to incoming atoms or molecules:

$$w^N(\mathbf{r}) = \frac{1}{k^2 T_{el}} \left[\frac{\partial n(\mathbf{r}, T_{el})}{\partial T_{el}} \right]_{v(\mathbf{r}), N} \tag{2}$$

$$\approx \frac{n(\mathbf{r}, T_{el}) - n(\mathbf{r}, 0)}{(kT_{el})^2}, \tag{3}$$

where N is the number of electrons in the system.

The local softness and the function $w^N(\mathbf{r})$ are closely related, as may be concluded already from their definitions in Eqs. (1) and (2). Below, a formal expression for the function $w^N(\mathbf{r})$ is presented showing this connection and the physical significance of $w^N(\mathbf{r})$ more clearly. We define in addition to the isoelectronic function $w^N(\mathbf{r})$ a function $w^\mu(\mathbf{r})$ by taking the derivative in Eq. (2) at constant Fermi level μ instead of at constant number of electrons. Both functions are related by

$$w^N(\mathbf{r}) = w^\mu(\mathbf{r}) - s(\mathbf{r}) \frac{W^\mu}{S}, \tag{4}$$

where $s(\mathbf{r})$ and S are the local and global softnesses and W^μ is the integral of $w^\mu(\mathbf{r})$ over space. Equation (4) shows that the integral of $w^N(\mathbf{r})$ over space is zero, as expected for an isoelectronic reactivity function. The density, $n(\mathbf{r}, T_{el})$, entering Eq. (3) may be expressed as the integral of the product of the Fermi function, $f(\epsilon)$, and the local Kohn-Sham density of states $g(\mathbf{r}, \epsilon)$ over the energy ϵ. In this paper we use the Fermi function at a nonzero auxiliary temperature, T_{el}. Applying the same techniques as has been described for the local softness in Ref. [7], the function $w^\mu(\mathbf{r})$ is the solution of an integral equation of the same structure as that derived for the local softness [6,7]

$$w^\mu(\mathbf{r}) = \int d^3\mathbf{r}' K^{-1}(\mathbf{r}, \mathbf{r}') i(\mathbf{r}'). \tag{5}$$

In the limit of zero electron temperature T_{el}, the kernel in Eq. (5) is the same response function as found for the local softness [7]. The source term $i(\mathbf{r})$

$$i(\mathbf{r}) = \frac{1}{k^2 T_{el}} \int d\epsilon \left(\frac{\partial f(\epsilon)}{\partial T_{el}} \right)_{v(\mathbf{r}), \mu} g(\mathbf{r}, \epsilon) \tag{6}$$

$$\xrightarrow{T_{el} \to 0} \frac{\pi^2}{3} \left(\frac{\partial g(\mathbf{r}, \epsilon)}{\partial \epsilon} \right)_{\epsilon = \mu} \tag{7}$$

is proportional to the energy derivative of the local density of states at the Fermi energy. Thus, the function $w^\mu(\mathbf{r})$ is essentially a (short-range) linear mapping of the energy derivative of the local DOS at the Fermi level. The local softness, on the other hand, is the same mapping, but applied to the local DOS at the Fermi level [6,7].

As mentioned in the introduction, the local softness measures the correlation between density fluctuations and fluctuations in the total number of electrons in a statistical ensemble [12,24]. In a grand-canonical ensemble, the reactivity index $w^N(\mathbf{r})$ has an interesting relationship to the correlation function between the density fluctuations and the fluctuations of the total energy of the surface:

$$w^N(\mathbf{r}) = \frac{1}{(kT_{el})^3} \left\{ \langle [H - \langle H \rangle][n(\mathbf{r}) - \langle n(\mathbf{r}) \rangle] \rangle \right.$$
$$\left. - \frac{s(\mathbf{r})}{S} \langle [H - \langle H \rangle][N - \langle N \rangle] \rangle \right\}, \tag{8}$$

where H is the Hamiltonian of the system and $\langle \rangle$ indicates the averaging over the grand-canonical ensemble.

The quantities $w^\mu(\mathbf{r})$ and $w^N(\mathbf{r})$ describe the spatial variation of the strength and the sign of the density change connected with low-energy excitations of the valence electrons. They represent essentially the difference of the densities of the LUMO's and HOMO's: Regions of positive values of $w^N(\mathbf{r})$ correlate to dominant spatial weight of unoccupied states and negative values to occupied states close to the Fermi level. Thus, the function $w^N(\mathbf{r})$ gives a *spatially resolved picture* of the essential information contained in the local density of states around the Fermi energy, which also forms the starting point for tight-binding-like models of the local reactivity [15–17]. Moreover, the concept underlying the definition of reactivity in Eq. (2) is flexible; different reactivity indices can be defined, incorporating weight functions other than the Fermi function used here for the occupation of Kohn-Sham eigenfunctions.

The determination of $w^N(\mathbf{r})$ requires two self-consistent calculations of the electron density for different electron temperatures T_{el} *without* changing the number of electrons in the system, a task readily performed. In contrast, the change of the electron temperatures at constant μ and *constant* external potential used defining $w^\mu(\mathbf{r})$ results in a change of the number of electrons per unit cell. The resulting charged systems cannot be treated within conventional supercell geometries. The finite difference formulation of Eq. (3) has, in addition, the advantage that it

enables the modeling of an increasing strength of the interaction of the adsorbate with the surface by increasing the value of T_{el}.

As an example of the applicability of $w^N(\mathbf{r})$ to the study of the reactivity of metal surfaces, we consider the interaction of a hydrogen molecule with the (100) surface of Pd. The calculations presented below were performed using DFT together with the generalized-gradient approximation (GGA) [25] and employing the full-potential linear-augmented plane wave method [26,27]. The parameters used in the calculation correspond to those used in Ref. [28]. The metal substrate is modeled by five layers separated by a 10 Å thick vacuum region.

The function $w^N(\mathbf{r})$ is displayed in Fig. 1 for clean Pd(100), calculated using $kT_{el} = 70$ meV and Eq. (3). The redistribution of electrons is quite pronounced. There is a clearly identifiable electron rearrangement within the d shell: The $(x^2 - y^2)$ electron density is increased [see Figs. 1(a) and 1(b) and the $(3z^2 - r^2)$ (see Figs. 1(c) and 1(d)] and (xy) orbitals [see Fig. 1(a)] are depleted. The $(x^2 - y^2)$ orbitals contribute to the bonding in the surface between the Pd atoms, which can be inferred from the fact that their band is rather wide and contains the highest number of unoccupied d states at the surface.

We now consider the dissociative adsorption of a hydrogen molecule on the Pd(100) surface in order to relate it to the reactivity index of Fig. 1. The DFT calculations [28] show that a H_2 molecule at a constant height, say at 1.8 Å above the center of the top Pd layer, experiences a significant corrugation of the potential energy as a function of its lateral position (when the H_2 center of mass is at 1.8 Å, the hydrogen wave functions extend up to $Z \approx 1.0$ Å): The potential energy for the H_2 center of mass at the hollow site is close to zero, at the bridge site it is attractive by 0.12 eV, and at the on-top site the attraction is 0.28 eV (see Ref. [28]). This corrugation can be inferred, at least qualitatively, from the w^N contour plot of Fig. 1: The strongest decrease of the surface electron density at distances between 1.0 and 1.5 Å occurs at the on-top site. Why does this strongest decrease of $w^N(\mathbf{r})$ parallel the highest attraction for the molecule? The dissociative adsorption of H_2 involves the breaking of the H-H bond and at the same time the formation of new hydrogen-surface bonds [17,28]. In a bond-orbital picture [17] hydrogen dissociation is nonactivated if the H_2 σ_g orbital as well as the σ_u interact with the d states, forming bonding states which are occupied, and if the corresponding antibonding orbitals remain essentially empty, i.e., if their DOS's lie essentially above the Fermi level. In particular, the partial occupation of the σ_u state destabilizes the H-H bond. It is quite plausible that this scenario is most effective at a site of the metal surface with a high density of d states just below the Fermi level, which means at regions with large negative values of $w^N(\mathbf{r})$. Indeed, the spatial distribution of $w^N(\mathbf{r})$ in Fig. 1(d) suggests that this region is at the on-top position. Here the H_2 molecule interacts strongly with the $(3z^2 - r^2)$ orbital of the surface Pd atom which gets partially depleted, and electrons are transferred into the $(x^2 - y^2)$ orbitals located in the surface plane.

Figure 2 displays DFT-GGA results for the interacting H_2-Pd(100) system; shown is the electron density *change* for a geometry with the hydrogen molecule at $Z = 1.8$ Å over the on-top position. This *change* is defined as the electron density of the H_2-Pd(100) system minus the density of the clean Pd(100) surface and minus the density of a H_2 molecules with the same bond length. It confirms the just-mentioned character of the interaction; in particular, the decrease of the occupation of the $(3z^2 - r^2)$ orbital of the surface Pd atom is clearly visible. All features in Fig. 2 are consistent with the spatial variation of
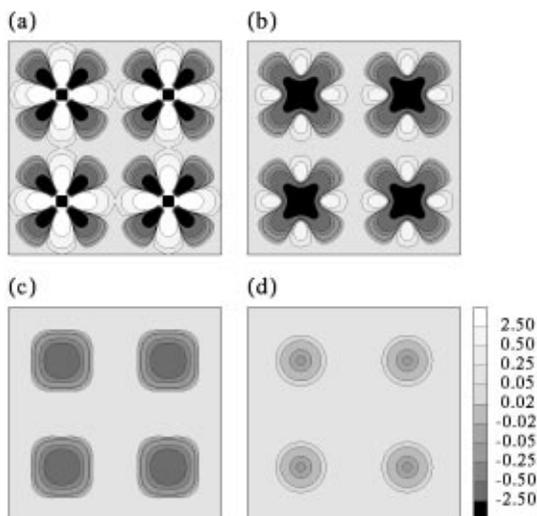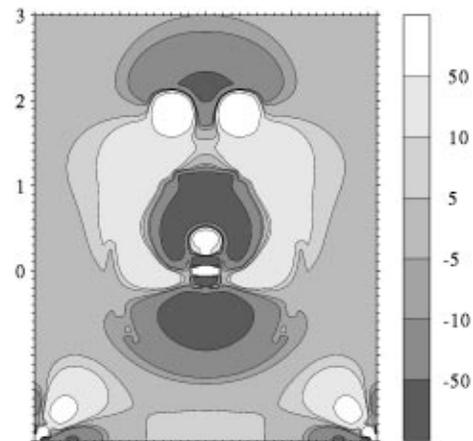

FIG. 1.   Contour plot of the function $w^N(\mathbf{r})$ for clean Pd(100) along planes parallel to the surface at different heights Z above the center of the surface Pd atoms: (a) $Z = 0$ Å, (b) $Z = 0.5$ Å, (c) $Z = 1$ Å, and (d) $Z = 1.5$ Å. Units are 10^{-1} Å^{-3} eV^{-2}.

FIG. 2.   Electron density change of a H_2 molecule above Pd(100) (see text) along the (0$\bar{1}$1) plane. The molecule is placed at a height $Z = 1.8$ Å above a surface Pd atom with the molecular axis parallel to the surface, and the two H atoms point toward hollow sites. Units are 10^{-3}/Å^3.
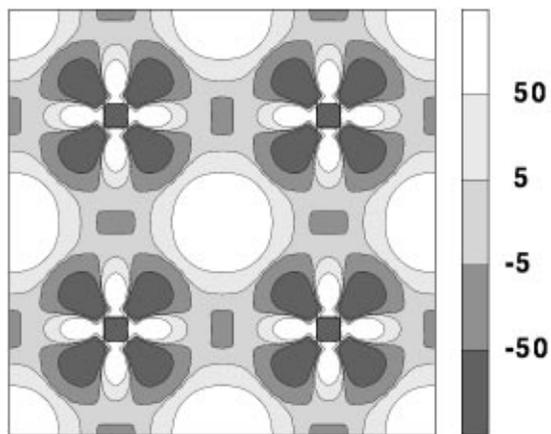
FIG. 3. Electron-density change at Pd(100) due to the adsorption of one monolayer of hydrogen at the surface hollow sites. The plane is the same as in Fig. 1(a); the units are $10^{-3}/\text{Å}^3$.

$w^N(\mathbf{r})$ and with the interpretation of hydrogen dissociation in terms of a tight-binding picture [17].

While the reactivity concept is based on perturbation theory [6] and can thus give quantitative information only for weakly interacting systems, it is not unreasonable to expect that for strong interactions the concept may still give *qualitatively* correct guidelines. Indeed, we find that for the chemisorption of atomic hydrogen at Pd(100) the function w^N can explain why the favorable adsorbate site is the fourfold hollow. The DFT calculations [29] of this chemisorption system tell that the hollow site adsorption is by about 0.3 eV more favorable than the bridge and 0.6 eV more favorable than the on-top site adsorption. Following the same lines as used for the discussion for the H$_2$ molecule, we expect that the H atom should prefer a site at which it has good overlap with dark (i.e., negative) sections of $w^N(\mathbf{r})$. Because of the smallness of the H atom, this is the hollow site (compare Fig. 1), in good agreement with the results of the DFT calculations of the interaction system. Figure 3 gives the calculated electron density change induced by a monolayer of H adatoms placed in the surface hollow sites. It compares surprisingly well with the prediction of the local polarization in Fig. 1(a). The comparison shows that the spatial variation of the function $w^N(\mathbf{r})$ is directly correlated with the shape of the electron polarization introduced by the adsorbed hydrogen.

In conclusion, the function $w^N(\mathbf{r})$ [see Eqs. (2) and (3)] of the clean surface is introduced as an isoelectronic reactivity index supplementing the local softness. It is closely related to the local polarizability of valence electrons induced by an atom or molecule chemically interacting with the surface. For the example of the dissociative adsorption of H$_2$ molecules on Pd(100), we show that the spatial variation of the function $w^N(\mathbf{r})$ allows rationalization of the preferred dissociation pathways as well as the preferred chemisorption sites of H adatoms. The above discussion was done for metal substrates. However, the same reasoning applies also for semiconductors and insulators.

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