Orbital Symmetry, Reactivity, and Transition Metal Surface Chemistry

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The local density of states (DOS), argued here to measure local chemical reactivity, becomes a powerful interpretive tool for surface chemistry when decomposed into components of different orbital symmetry. We compute the symmetry- and layer-resolved DOS for Pd(001) and Rh(001) and use the results to generalize the Harris-Andersson theory of chemisorption, to interpret Feibelman's findings on the interaction of H_2 with the Rh(001) surface, and to interpret the preference of atomic H for the fourfold hollow sites of fcc (001) transition metal surfaces.

The detailed, quantitative understanding of surface chemistry on solids—chemisorption, corrosion, catalysis, etc.—is not yet fully within our grasp. Such understanding could be based on the accurate computation from first principles of total energies, or free energies, as, e.g., functions of a reaction coordinate. The difficulty arises from the fact that those computational techniques which are efficient for molecules are quite different from those which are efficient for solid surfaces. The problem is especially difficult for metals, which, having a finite density of states for vanishing excitation energy, are highly deformable locally, i.e., soft in the chemical sense [1]. While progress is underway in computational surface chemistry (cf., e.g., Refs. [2–4]), a quantitative measure of the local chemical reactivity of a metallic surface which is calculable from the properties of the metal alone and which expresses quantitatively this local deformability would be most useful.

There is now a highly developed theory of the chemical reactivity of molecules. It is based largely on Fukui's concept of frontier orbitals, the lowest unoccupied molecular orbital (LUMO), and the highest occupied molecular orbital (HOMO) [5]. Articulated originally within an approximate theory, the concept has been reexpressed by Parr and collaborators within an exact framework provided by the density functional formulation of many-electron theory [1] (see also Ref. [6]). Hoffmann [7] has shown within an approximate framework how the reactivity theory applies to chemistry at surfaces and, in particular, to chemisorption. In the present paper, we give the reactivity theory a particularly simple form, relating the reactivity directly to the Kohn-Sham local density of states (DOS) [8,9]. This form is much in the spirit of Hoffmann's arguments and is especially convenient for understanding the chemical activity of transition metal surfaces, as we illustrate here for the Rh(001) and Pd(001) surfaces via self-consistent, surface Green's-function computations based on the tight-binding, linear-muffin-tin-orbital (TB-LMTO) theory [10,11]. The implications of

the local DOS emerge most clearly after its decomposition into the contributions of the various orbital symmetries, which we present here for the first time. We then use the results of the decomposition to put the Harris and Andersson [12] interpretation of dissociation energies of H_2 on transition metals on a sound footing and to provide a simple, elegant interpretation of Feibelman's surprising finding that the most favorable location for the approach of H_2 to the Rh(001) surface is not a site of high symmetry [2]. Finally, similar arguments provide a convincing interpretation of the preference of H atoms for the fourfold hollow sites of fcc transition metal surfaces [3,13].

The chemical reactivity of a molecule has been characterized by the local softness $s(\mathbf{r})$ [14],

$$s(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_{v(\mathbf{r})}. \tag{1}$$

In Eq. (1) $\rho(\mathbf{r})$ is the electron density, μ is the chemical potential or Fermi level, $v(\mathbf{r})$ is the total nuclear potential acting on the electrons at point $\mathbf{r}$, the partial derivative with respect to μ is taken for fixed $v(\mathbf{r})$ viewed as an external potential, and, for metals, no distinction need be made between changes of μ which increase or decrease the total number of electrons. The quantities $\rho(\mathbf{r})$ and μ are given exactly in the Kohn-Sham formulation of density funtional theory [8], and $\rho(\mathbf{r})$ is related to μ by

$$\rho(\mathbf{r}) = \int^{\mu} g(E, \mathbf{r})\, dE, \tag{2}$$

where $g(E, \mathbf{r})$ is the local Kohn-Sham density of states. Thus, the local softness is simply

$$s(\mathbf{r}) = g(\mu, \mathbf{r}) + \int^{\mu} \left[\frac{\partial g(E, \mathbf{r})}{\partial \mu}\right]_{v(\mathbf{r})} dE. \tag{3}$$

Yang and Parr [15] found the first term in (3) but not the second and, identifying $s(\mathbf{r})$ with $g(\mu, \mathbf{r})$, were the first to establish a relationship between them based on density
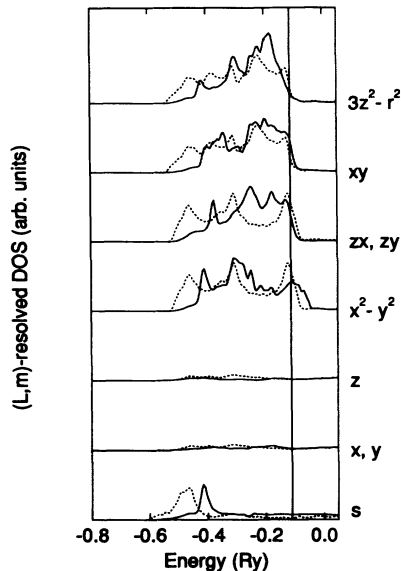
FIG. 1. Orbital-resolved DOS's for the top sample layer ($s1$) of Pd(001). The corresponding results for the bulk (dotted line) are shown. The vertical line denotes the position of the bulk substrate Fermi level.
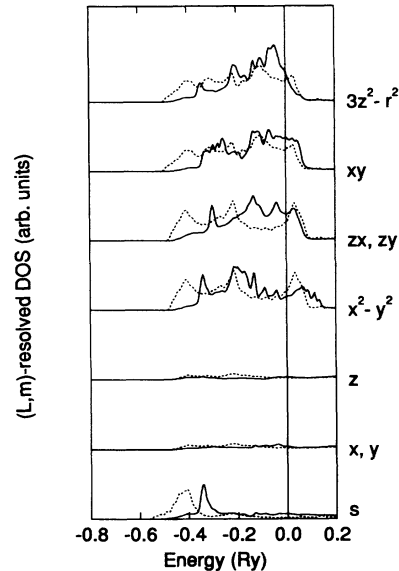

FIG. 2. Orbital-resolved DOS's for the top sample layer ($s1$) of Rh(001). The corresponding results for the bulk (dotted line) are shown. The vertical line denotes the position of the bulk substrate Fermi level.

functional theory. Equation (3) can be solved explicitly for $s(\mathbf{r})$ [16],

$$s(\mathbf{r}) = \int d\mathbf{r}'\, K^{-1}(\mathbf{r}, \mathbf{r}')\, g(\mu, \mathbf{r}'). \tag{4}$$

We have shown [16] that $K(\mathbf{r}, \mathbf{r}')$ is the transpose of a response function $\kappa(\mathbf{r}, \mathbf{r}')$ which asymptotically approaches the Hartree approximation to the static Kohn-Sham dielectric function $\epsilon_H(\mathbf{r}, \mathbf{r}')$. Thus the electronic softness $s(\mathbf{r})$ can be regarded as a response to the local density of states at the Fermi level. Moreover, we have introduced nuclear reactivities [16] as the quantities most fundamental to an understanding of chemical reactivity. The softness of a particular nucleus a, σ_a, is the derivative of the force on that nucleus with respect to μ. We have shown that σ_a is linearly related to $g(\mu, \mathbf{r})$ via the electron-nuclear Coulomb force screened by $\kappa(\mathbf{r}, \mathbf{r}')$ so that the nuclear softness can also be regarded as a response to the local density of states at the Fermi level. Thus $g(\mu, \mathbf{r})$ is fundamental to chemical reactivity, electronic or nuclear.

$K^{-1}(\mathbf{r}, \mathbf{r}')$ differs substantially from $\delta(\mathbf{r}, \mathbf{r}')$ and $s(\mathbf{r})$ accordingly from $g(\mu, \mathbf{r})$. $s(\mathbf{r})$ in fact is a local average of $g(\mu, \mathbf{r})$ with a position dependent change of scale. Nevertheless, we do not expect conclusions concerning chemical reactivity drawn from $g(\mu, \mathbf{r})$ to differ significantly from those drawn from $s(\mathbf{r})$.

This essentially conventional definition of softness is not sufficient for our purposes because we deal with continuous bands of levels and not the isolated levels of atoms or molecules. The problem of how to weight the contributions of the various regions of the band struc-

ture is as yet unsolved. Nevertheless, it is clear from the formal structure of the Kohn-Sham theory that the local density of states $g(E, \mathbf{r})$ must play a central role in the appropiate generalization of the local softness just as $g(\mu, \mathbf{r})$ does in Eq. (4). In fact, $g(E, \mathbf{r})$ has long played a prominent role in discussions of the chemistry of solids, either explicitly or implicitly, and the above arguments provide a much deeper justification of its use. We here present three illustrations of its power as an interpretive tool in surface chemistry.

More convenient than $g(E, \mathbf{r})$ for our purposes is its projection $g_\nu(E)$ onto the TB-LMTO basis set within which our computations [10,11] are carried out (cf. Hoffmann [7]). Here ν is a composite index specifying the position of an atom within the 2D unit cell of a given layer p and symmetry type $(l, m) = s, x, y, z, xy, yz, zx, x^2 - y^2, 3z^2 - r^2$ of the TB LMTO. For an fcc metal bounded by an (001) plane for which all atoms in a given layer are equivalent, p reduces to the layer number. We have calculated $g_\nu(E)$ from first principles in the local density approximation [11] and show the results in Fig. 1 for the surface layer of Pd(001) and in Fig. 2 for Rh(001). To see why the full $g_\nu(E)$ is necessary, first consider the explanation given by Harris and Andersson [12] for the fact that H_2 is not chemisorbed on the noble metals but is chemisorbed, with reduced or eliminated activation energy, on the neighboring transition metals. As a molecule approaches the surface of a noble metal it first encounters the tails of the metallic electron density and experiences an increasing Pauli repulsion which prevents the close approach needed for chemisorption. According to Harris and Andersson (HA) [12], this Pauli repulsion is elimi-

TABLE I. Partial and total contributions to the valence charge of a Pd atom for a Pd(001) surface and in bulk Pd. The top three layers are denoted by $s1$, $s2$, and $s3$, while vacuum refers to the solid-vacuum interface layer.

	Vacuum	$s1$	$s2$	$s3$	Bulk
s	0.1182	0.5136	0.5834	0.5873	0.5844
x, y	0.0252	0.1473	0.2070	0.2086	0.2097
z	0.0449	0.0936	0.2077	0.2109	0.2097
p	0.0953	0.3882	0.6217	0.6280	0.6291
$x^2 - y^2$	0.0047	1.5777	1.6946	1.6992	1.6945
yz, zx	0.0136	1.7924	1.6863	1.6902	1.6945
xy	0.0077	1.8185	1.8665	1.8495	1.8515
$3z^2 - r^2$	0.0088	1.8594	1.8577	1.8536	1.8515
d	0.0484	8.8404	8.7914	8.7827	8.7866
Total	0.2619	9.7422	9.9965	9.9980	10.0000

TABLE II. Partial and total contributions to the valence charge of a Rh atom for a Rh(001) surface and in bulk Rh. The top three layers are denoted by $s1$, $s2$, and $s3$, while vacuum refers to the solid-vacuum interface layer.

	Vacuum	$s1$	$s2$	$s3$	Bulk
s	0.1509	0.5275	0.6034	0.6066	0.6027
x, y	0.0302	0.1691	0.2387	0.2419	0.2439
z	0.0538	0.1065	0.2410	0.2454	0.2439
p	0.1142	0.4447	0.7185	0.7292	0.7317
$x^2 - y^2$	0.0060	1.4043	1.4721	1.4330	1.4407
xz, yz	0.0155	1.5248	1.4294	1.4416	1.4407
xy	0.0077	1.5444	1.6552	1.6840	1.6717
$3z^2 - r^2$	0.0107	1.7119	1.6902	1.6613	1.6717
d	0.0554	7.7102	7.6763	7.6615	7.6655
Total	0.3205	8.6824	8.9981	8.9973	9.0000

nated in the transition metals by transfer of the electrons in the tail inward into the high local density of empty d states. Thus, the local capacity to absorb the displaced electrons depends not simply on $g_\nu(\mu)$ but on the total number of locally available d holes, an integral over $g_\nu(E)$.

We have calculated the total number of electrons per atom in each layer and of each symmetry type n_ν, with the results shown in Tables I and II. These local quantities play the role of Fukui's HOMO for metals. In our calculations, the tails of the wave functions are captured in the vacuum layer, where they are artificially decomposed into s, p, and d functions centered within that layer. What is important, therefore, is the total number of electrons in the vacuum layer.

Thus, in the HA mechanism, as much as $0.26e$ per atom may have to be displaced from the vacuum for Pd and $0.32e$ for Rh. The local capacity of the d band to accept electrons is measured by the quantities

$$h_\nu = \int_\mu^{E_\nu} g_\nu(E)\, dE, \qquad (5)$$

where E_ν is the d-band edge for layer p and symmetry type (l, m), the quantities playing the role of Fukui's LUMO. Apart from the complexities introduced by hybridization with the d parts of the plane-wave-like states, the h_ν are readily estimated from $2 - n_\nu$.

Harris and Andersson did not distinguish among the various local d states. However, by doing so, we are able to understand via their mechanism the finding of Feibelman [2] that H_2 is most strongly attached to the Rh(001) surface when its molecular axis is parallel to the surface and the H atoms are above positions within the triangle formed by one Rh atom and two of its nearest neighbors and are aimed at adjacent bridge sites [cf. Fig. 1(c) of Ref. [2]], vs having the molecular center above a bridge site with the molecular axis perpendicular [Fig. 1(a) [2]] or parallel [Fig. 1(b) [2]] to the bridge axis.

Note that the charge countour plots displayed by Feibelman in his Fig. 1 are in a plane in our vacuum

layer 2.98 bohrs above the outer Rh nuclei with the H nuclei residing at a height of 3.98 bohrs. One can infer from Fig. 1 [2] the principal features of the unperturbed electron density at 2.98 bohrs. There are minima at the fourfold hollow sites and maxima above the Rh nuclei. This pattern is precisely what is implied by the values of the n_ν of the vacuum layer in Table II.

In the HA mechanism, the electron density of the H_2 molecule initially simply adds to the unperturbed electron density of the metal. The expected changes of electron density thus introduced are consistent with those found by Feibelman (Fig. 1 of Ref. [2]), a filling in of adjacent minima and merging of the H_2 contours with those around adjacent maxima. The Pauli repulsion thus produced then drives electron promotion from the vicinity of the H_2 inward into the empty surface d orbitals in the HA mechanism, a higher-order effect. Feibelman's finding that H_2 is most strongly attached to the surface in the case shown in his Fig. 1(c) gives strong evidence for the operation of the HA mechanism. Without the latter, one would expect maximum attraction to occur for a geometric configuration that minimizes the overlap of electron densities and thereby the Pauli repulsion. That minimum would occur above the hollow site with the molecular axis parallel to the square edge, $\langle 10 \rangle$ or $\langle 01 \rangle$, where the metallic electron density is minimal.

Transferring electrons from the vacuum into the surface d orbitals which extend perpendicular to the surface, i.e., the xz, yz, and $3z^2 - r^2$ orbitals, does not mitigate the Pauli repulsion as much as transferring electrons into the xy and $x^2 - y^2$ orbitals, which extend along the surface. $h_{x^2-y^2} + h_{xy}$ equals 0.60 for Pd and 1.06 for Rh per surface atom, providing ample capacity for the HA mechanism. Transferring electrons only into the empty xy states creates additional ridges of electron density along the diagonals of the surface unit cell, the $\langle 11 \rangle$ and $\langle 1, \bar{1} \rangle$ directions, making these unfavorable locations for the H_2 molecule. Transferring electrons only into $x^2 - y^2$ states creates additional ridges of electron density along the $\langle 10 \rangle$ and $\langle 01 \rangle$ directions making these unfavorable lo-

cations as well. Our extension of the Harris-Andersson picture implies that charge has been transferred to xy orbitals of the Rh atoms at the ends of the bridge to minimize the Pauli repulsion for the cases of Figs. 1(a) and 1(b) of Ref. [2]. The case of Fig. 1(c) corresponds to charge transfer into the $x^2 - y^2$ states of the (0,1) atom and the xy states of the (0,0) and (1,1) atoms neighboring the H_2 molecule. By distributing the promoted charge primarily over three atoms in the latter case versus primarily over two atoms in the former, a greater reduction of the Pauli repulsion occurs, possibly accounting for the latter being the favored location and orientation [2]. Clearly, the HA mechanism does not operate in a noble metal with a filled d band, and there is no reason there to expect the configuration of Fig. 1(c) to be most favorable for dissociation.

Finally, we consider the finding of Wilke et al. [3] that H atoms prefer the fourfold hollow sites of the Pd(001) surface, a preference that is shared by Rh(001) [13] as well as other transition metals [17]. The first step is to recognize that the TB-LMTO basis provides a representation of the Hamiltonian and Green's function which is analogous to that of a simple tight-binding representation, but, of course, much more rapidly convergent [18]. Thus arguments similar to those developed by Grimley [19] can be given a much more nearly rigorous basis [20]. Because of the large ionization energy of the H atom, the states which would hybridize most strongly are the d states of lowest energy in the surface layer. These, according to Figs. 1 and 2, are first the $x^2 - y^2$ and next the xy states. However, for hybridization to lead to bonding, the resulting antibonding states should lie mostly above the Fermi level so that the most favorable d states are not necessarily the lowest. It is possible, therefore, that the xy states are more favorable in this respect than the $x^2 - y^2$. The chemisorption energy depends as well on the magnitude of the hybridization integral and on the number of neighbors. While the hybridization integral is larger for the bridge site ($x^2 - y^2$) than it is for the hollow site (xy), the number of neighbors is 4 for the latter and 2 for the former. Thus the dominant factors in stabilizing the hollow site are first the larger number of neighbors and second the possibly optimal location in energy of the xy subband structure.

We conclude that projecting the local DOS onto the TB LMTO basis set provides a powerful set of interpretive tools for understanding both experimental and theoretical results in surface chemistry, making contact with current theories of chemical reactivity in their most general form as well.

This work is part of the program of the Consortium on "The Physical Aspects of Surface Chemistry on Metals,

[1] R.G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules (Oxford University Press, New York, 1989).

[2] P.J. Feibelman, Phys. Rev. Lett. 67, 461 (1991).

[3] S. Wilke, D. Hennig, R. Löber, M. Methfessel, and M. Scheffler (to be published).

[4] B. Hammer, K.W. Jacobsen, and J.K. Norskov, Phys. Rev. Lett. 70, 3971 (1993).

[5] K. Fukui, T. Yonezawa, and H. Shingu, J. Chem. Phys. 20, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, J. Chem. Phys. 22, 1433 (1954); K. Fukui, Theory of Orientation and Stereoselection (Springer-Verlag, Berlin, 1975); K. Fukui, Science 218, 747 (1987).

[6] M. Galvan, A. Dal Pino, Jr., and J.D. Joannopoulos, Phys. Rev. Lett. 70, 21 (1993).

[7] R. Hoffmann, Rev. Mod. Phys. 60, 601 (1988).

[8] W. Kohn and L. Sham, Phys. Rev. 140, A1133 (1965); R.M. Dreizler and E.K. Gross, Density Functional Theory (Springer-Verlag, Berlin, 1990).

[9] The reactivity of a molecule has been related to the Kohn-Sham wave functions by W. Yang, R.G. Parr, and R. Pucci, J. Chem. Phys. 81, 2862 (1984).

[10] J. Kudrnovský, I. Turek, V. Drchal, P. Weinberger, N.E. Christensen, and S.K. Bose, Phys. Rev. B 46, 4222 (1992).

[11] M.V. Ganduglia-Pirovano, J. Kudrnovský, I. Turek, V. Drchal, and M.H. Cohen, Phys. Rev. B 48, 1870 (1993).

[12] J. Harris and S. Andersson, Phys. Rev. Lett. 55, 1583 (1985).

[13] P. Feibelman, Phys. Rev. B 43, 9452 (1991).

[14] Ref. [1], p. 101ff.

[15] W. Yang and R.G. Parr, Proc. Natl. Acad. Sci. U.S.A. 82, 6723 (1985).

[16] M.H. Cohen, M.V. Ganduglia-Pirovano, and J. Kudrnovský (to be published).

[17] K. Christmann, Surf. Sci. Rep. 9, 1 (1988).

[18] J. Kudrnovský, I. Turek, V. Drchal, P. Weinberger, S.K. Bose, and A. Pasturel, Phys. Rev. B 47, 16525 (1993).

[19] T.B. Grimley, Prog. Surf. Sci. Membrane Sci. 9, 118–119 (1975). See also, J. Kudrnovský and B. Velický, Czech. J. Phys. B 35, 1017 (1985).

[20] This is another instance of the need for the full $g_\nu(E)$ to characterize reactivity.