Surface Density of States on Crystalline
Transition Metal Substrates*

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The local density of states on the (100) surface of an FCC tight-binding solid has been determined for an s-band and for a d-band model. Effects due to chemisorption are also treated for the s-band simple cubic substrate.

To understand the electronic structure of clean transition metal surfaces, as well as the interaction of adsorbates with such surfaces, we have been studying the local density of states (DOS) of LCAO models. While inter-electronic correlations are no doubt important in such problems, we believe considerable insight can be gained from such simple one-electron models.[1]

Beginning with the clean surface, we consider localized basis functions $\varphi_{i\mu}$ of symmetry type μ located at site i. For example, $\varphi_{i\mu}$ could be a Wannier-like function analogous to atomic s, p, or d functions. The matrix elements of the substrate Hamiltonian H_o in this site representation are

$$\langle i\mu|H_o|i\mu\rangle \equiv \varepsilon_{i\mu} \qquad (1a)$$

$$\langle j\mu'|H_o|i\mu\rangle \equiv t_{j\mu'i\mu}. \qquad (1b)$$

While ultimately these matrix elements must be determined self-consistently, we initially take $\varepsilon_{i\mu}$ to be site independent and $t_{j\mu'i\mu}$ to be only a function of the relative position $R_i - R_j$ for given μ and μ'. We use the Green's function method of Kalkstein and Soven[2] to determine the local density of states $\rho_{i\mu}(E)$ of H_o. By definition,

$$\rho_{i\mu}(E) = \sum_n |\langle i\mu|n\rangle|^2 \delta(E-\varepsilon_n) = \frac{1}{\pi} \operatorname{Im} G_{i\mu i\mu}(E), \qquad (2)$$

where $|n\rangle$ and ε_n are the eigenvectors and eigenvalues of H_o, and

$$G(E) = (E - H_o - i\delta)^{-1}, \ (\delta = 0^+) \qquad (3)$$

The bulk and surface local DOS (ρ_b and ρ_s) for the (100) surface of an FCC s-band crystal

are shown in Fig. 1, using the bulk Green's functions of Frikkee.[3] Only nearest neighbor hopping is included. At the surface, the peak in ρ_b is strongly shifted toward the center of the band leading to a band narrowing, consistent with the second moment relation

$$M_{i\mu}(2) \equiv \int_{-\infty}^{\infty} (E-\varepsilon_{i\mu})^2 \rho_{i\mu}(E) \, dE = \sum_{j\mu'} |t_{j\mu'i\mu}|^2, \qquad (4)$$

since the number of nearest neighbors is reduced by a factor of 2/3 at the surface.

For the FCC (100) d-band case, taking z as the positive normal to the surface, we consider the five d-functions having symmetry xy, yz, zx, $x^2 - y^2$ and $3z^2 - r^2$ on each site. Considering again only nearest neighbor hopping, symmetry reduces $t_{j\mu'i\mu}$ to

$$t_{j\mu'i\mu} = \alpha t_\sigma + \beta t_\pi + \gamma t_\delta, \qquad (5)$$

where t_m corresponds to hopping between orbitals of magnetic quantum number $m = 0, 1, 2$ along the symmetry axis joining i and j.
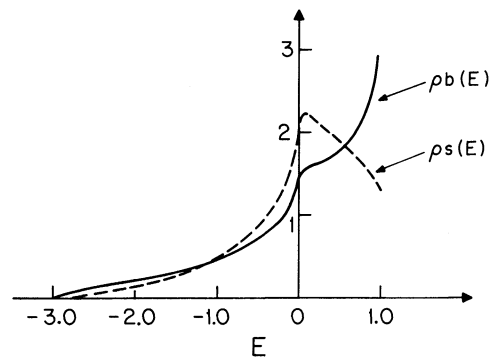

Fig. 1. The bulk and surface density of states, ρ_b and ρ_s, plotted as a function of energy for the (100) surface of a face-centered cubic s-band solid. The bulk band width is chosen to be 4 units of energy, corresponding to a nearest neighbor hopping of $-1/4$.
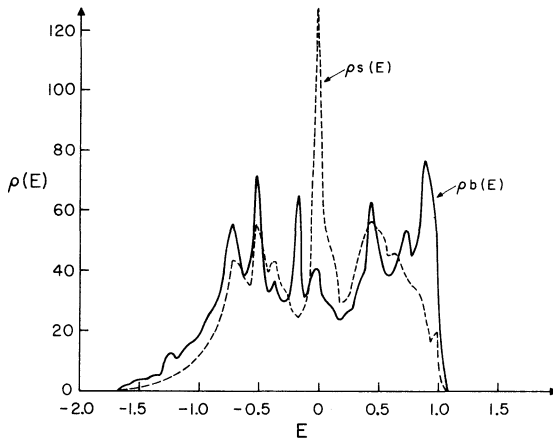
Fig. 2. The total bulk and surface density of states for the (100) surface of an FCC d-band solid. Parameters are chosen to fit the bulk band of Ni. Self-consistency effects affect these results, as discussed in the text.

α, β and γ have been tabulated by Slater and Koster.[4] Estimates of t_m can be obtained from an LCAO fit to the bulk band structure. For Ni one finds[4] $t_\sigma = -0.338$ eV, $t_\pi = +0.182$ eV, and $t_\delta = -0.026$ eV. Using these values, one obtains the results of Fig. 2 for the total d-band density of states.[5] The large DOS near the top of the bulk band, arising mainly from the xy, yz and zx orbitals, is again shifted toward the band center. However, the orbitally projected surface DOS, $\rho_{s\mu}$, shows that the main narrowing effects occur for the "out of plane" functions, yz, zx and $3z^2 - r^2$ which stick out from the surface, while the "in plane" functions, xy and $x^2 - y^2$, are much less affected. These results are consistent with the second moment relations (4) since, for example, the yz function, lying mainly in the yz plane, loses half of its important nearest neighbors at the surface, while the xy function loses none.

It is clear that self-consistency effects can be very important in determining $\rho_{s\mu}$. For Ni, if one uses the above $\rho_s(E)$ with the Fermi level fixed by the bulk, the bulk hole count of roughly 0.6 is reduced to approximately 0.2 at the surface since the out of plane orbitals yz and zx are nearly filled (rather then having 0.2 holes as in the bulk). This would lead to an increase of $\varepsilon_{i\mu}$ on the surface plane by several eV, thereby raising and distorting $\rho_{s\mu}(E)$ so that the total surface hole count would return to approximately its bulk value. An essential difference is that at the surface the holes are no longer

equally shared amongst the t_{2g} orbitals (xy, yz and zx) but are concentrated somewhat into the xy-orbital. Furthermore, the increase of $\varepsilon_{s\mu}$ can lead to an increased peaking of $\rho_{sxy}(E)$ at the top of the band, and for sufficiently large $\varepsilon_{s\mu}$ a surface state of xy symmetry will split off from the top of the d-band. Although delta-function-like in this model, the actual split-off state would be broadened by hybridization with the s-p background. At present, it is unclear if this split off state occurs at self-consistency.

It would be interesting to test the above results with field emission as well as angle and energy resolved photoemission experiments, since the in plane and out of plane orbitals enter quite differently in the matrix elements for these processes.

Turning to the influence of adsorbates on the density of states, we again note the probable importance of correlation effects, particularly between electrons in adorbitals of light atoms. For heavy adatoms or for admolecules, these effects may be less important. For simplicity we assume here that the one electron description of the system is appropriate. We consider a single adorbital φ_a orthogonal to the substrate orbitals and having site-diagonal energy E_a. Let φ_a couple to the group orbital φ_x which is the appropriate symmetry combination of substrate orbitals at the adsorption site and let

$$\langle x|H|a\rangle \equiv V_x. \tag{6}$$

For example, if an s-state adorbital is atop of a single substrate atom labelled 1, $\varphi_x = \varphi_{1d_{z^2}}$, etc.

The change in the total DOS (for one spin direction) is

$$\Delta\tilde{\rho}(E) = \frac{1}{\pi}\frac{\partial}{\partial E}\text{Im}\ln\left(1 - V_x^2 G_{aa}(E)G_{xx}(E)\right)$$
$$+ \delta(E - E_a), \tag{7}$$

where the last term is added to cancel the free atom DOS for convenience of plotting. The integral of $\Delta\tilde{\rho}$ over all E is unity. In this expression $G_{aa}(E) = (E - E_a - i\delta)^{-1}$ and $G_{xx}(E) = \langle x|(E - H_o - i\delta)^{-1}|x\rangle$, where π^{-1} Im $G_{xx}(E)$ is the group orbital DOS for the clean surface. The present calculations were carried out for an s-band simple cubic (100) substrate and adsorption atop of a single atom 1. The local surface DOS can be found in ref. 2. and in Fig. 4

Figure 3 shows $\Delta\tilde{\rho}(E)$ for several values of V,
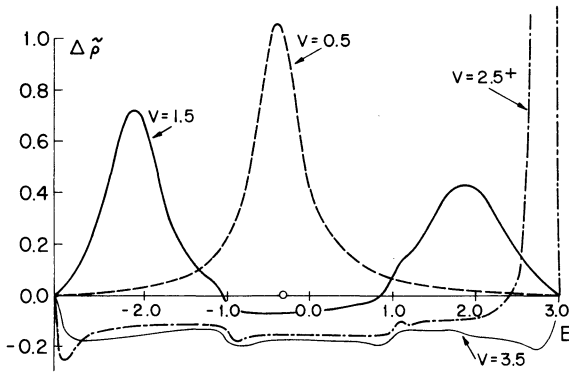
Fig. 3. Change of total density of states on adsorption of an atom on the (100) surface of a simple cubic *s*-band solid, for several values of *V*. Split off states are not shown. The small circle denotes E_a.
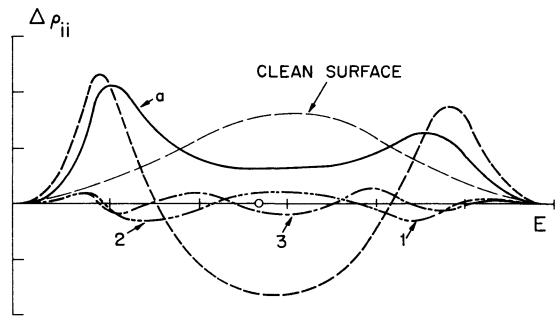

Fig. 4. The change of local density of states for the adsorbate, the atom 1 to which *a* is coupled, and for the nearest neighbor (2) and next nearest neighbor (3), of atom 1 in the surface plane. Also shown is the density of states for the clean surface. The arrow from the label "1" on the figure should point to the left rather than up; the dashed curve describes the change on atom 1.

with E_a fixed near the center of the band.[7] We choose units in which the band width in 6 (i.e. the tight-binding hopping parameter is $-1/2$). For weak $V(=0.5)$ the delta function at E_a broadens to a Lorentzian whose width is proportional to V^2. For an intermediate value of $V(=1.5)$ the E_a resonance splits into a bonding and an antibonding resonance, while for large $V(=2.504)$ a narrow antibonding resonance occurs at the upper band edge and a bonding state is barely split off from the bottom of the band. For very large V, except for the split off states, $\Delta\tilde\rho$ is insensitive to V, corresponding to a solid with a missing orbital φ_1, i.e. a surface vacancy, and with φ_1 and φ_a combining to form the bonding and antibonding states of a surface complex. For systems of physical interest, V is roughly 1.5 to 2.5.

The total change in density of states $\Delta\tilde\rho$ can be decomposed into ρ_{aa} and changes substrate local DOS $\Delta\rho_{ii}$:

$$\Delta\tilde\rho = \rho_{aa}(E) + \sum_i \Delta\rho_{ii}(E). \qquad (8)$$

Fixing attention on $V = 1.5$ so that all of $\Delta\tilde\rho$ lies within the band, we ask how the $\Delta\rho_{ii}$'s drop off away from the adsorption site. One finds

$$\rho_{aa}(E) = \frac{1}{\pi} \operatorname{Im} \mathscr{G}_{aa}(E) \qquad (9)$$

where

$$\mathscr{G}_{aa}(E) = [E - E_a - V^2 G_{11}(E)]^{-1}.$$

Also

$$\Delta\rho_{ii} = \frac{1}{\pi} \operatorname{Im} V^2 \mathscr{G}_{aa}(E) G_{1i}^2(E), \qquad (10)$$

where G_{1i} is the Green's function for the clean substrate, $\langle 1|[E - H_o - i\delta]^{-1}|i\rangle$. In Fig. 4 we see that the sum of ρ_{aa} and $\Delta\rho_{11}$ give the double peak structure of $\Delta\tilde\rho$. The illustrated absence of the two peak structure in the change of DOS of the atoms in the surface plane which are nearest and next-nearest neighbors of atom 1 (and in all other $\Delta\rho_{ii}$ as well) shows that the bonding and antibonding resonances are well localized on orbitals *a* and 1 even if no split off states occur, supporting the picture of a surface complex.

To see how $\Delta\rho_{ii}$ drops off into the bulk, we note that for a simple cubic *s*-band substrate the sum of $\Delta\rho_{ii}$ over all atoms in the mth layer goes as the imaginary part of the product of $V^2 \mathscr{G}_{aa}$ and a single substrate Green's function. As Fig. 5 shows, $\Delta\rho_m$ decreases fairly rapidly, having a rapid and varied wiggle structure by the third and fourth planes. This disturbance of $\Delta\rho_{ii}$ away from the surface should influence the fine structure of the photoemission differ-
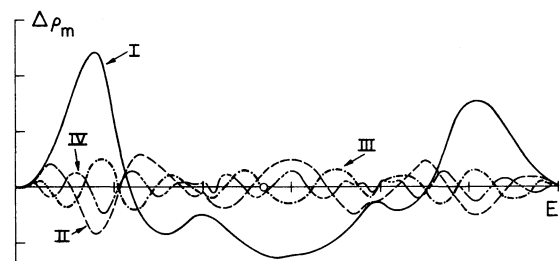

Fig. 5. Change of total density of states on the first (I), second (II), third (III), and fourth (IV) planes.

ence spectra since one varies the depth being sampled as one varies energy and/or collection angle. We note that in photoemission theory, the off-diagonal DOS $\Delta\rho_{ij}$ also enters; however, hemispherical averaging reduces significantly these interference effects and the above discussion should be qualitatively correct.

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