CHANGES IN DENSITY OF STATES CAUSED BY CHEMISORPTION, WITH IMPLICATIONS FOR PHOTOEMISSION *

Considerable effort has recently been devoted to investigating the changes in photoemission from transition metals when light gas atoms (H, O, N, C, etc.) are absorbed on their surfaces[1,2]. We can gain insight into the features of the changes by investigating the change in electronic density of states (Δ DOS) using the framework presented by Einstein and Schrieffer[3] (hereafter denoted by ES). This one-electron model provides a simple way to visualize the formation of peaks below the d-band, the depletion of states within the center of the band, and the general dependence of spectra on the natural parameters of the problem.

The model of ES considers the (100) surface of a single s-band, simple cubic, semi-infinite lattice in the tight-binding approximation [(100) cubium], as treated by Kalkstein and Soven[4]), and Allan[5]), with the one-center matrix element set at zero; the center of the bulk band is the energy zero. We take the two-center matrix element to be $-\frac{1}{2}$, which sets the energy scale and gives a bandwidth of 6. We represent the adatom by a single, sharp, non-degenerate (save for spin) level of energy E_a. The best rough estimate of E_a is an average of the ionization (I) and affinity (A) levels, rather than simply the former. The model is most realistic for neutral adsorption, i.e. when E_a and the Fermi energy are relatively close, and when the Coulomb interaction ($\sim I-A$) is not too large. The perturbation parameter, V, characterizes the hopping of an electron between an adatom and its nearest neighbor on the substrate, as in the Anderson model[6]). For clarity and brevity, our presentation assumes that the adatom sits directly above a surface atom in the atop position. The present discussion neglects self-consistency effects; we are presently implementing them[7]). We note here, however, that for atop binding, particle–hole symmetry gives self-consistency automatically for a half-filled band and $E_a = 0$. We will therefore keep E_a near the band center even though this may tend to overemphasize adatom–substrate mixing.

For a single adatom on the surface, the total ΔDOS for a particular spin direction is[3])

$$\Delta\rho = \rho - \rho^0 = \pi^{-1} \operatorname{Im} \frac{\partial}{\partial E} \ln \left[1 - V^2 G_{aa}(E) G_{11}(E)\right], \qquad (1)$$

where $G_{aa} = (E - E_a - i\delta)^{-1}$ and G_{11} is the 11 diagonal component in a site representation of the Green's function for (100) cubium, 1 denoting the atom beneath the adatom; ρ is the DOS for the adsorbed system while $\rho^0 = \pi^{-1} \operatorname{Im} (G_{aa} + \sum_i G_{ii})$ is the DOS of the semi-infinite bulk plus the free atom. Since the unperturbed DOS contains a delta-function peak at E_a, we shall dispay

$$\Delta\tilde{\rho} = \Delta\rho + \delta(E - E_a). \qquad (2)$$

This is also the quantity of experimental interest since photoemission difference spectra are obtained by subtraction of the clean surface spectrum from the adsorbate–substrate system spectrum, with the free adatom neglected. Notice that $\Delta\tilde{\rho}$ satisfies the electron-conservation sum rule

$$\int_{-\infty}^{\infty} \Delta\tilde{\rho}(E)\, dE = 1, \qquad (3)$$

which corresponds to the statement that the perturbing potential is off-diagonal so that the trace of the perturbed hamiltonian is the same as that of the unperturbed one. From second-order perturbation theory, we expect a "repulsion" between E_a and the levels of the bulk, so that the DOS will shift away from E_a. Fig. 1 verifies this behavior of $\Delta\tilde{\rho}(E)$ for several values of V,
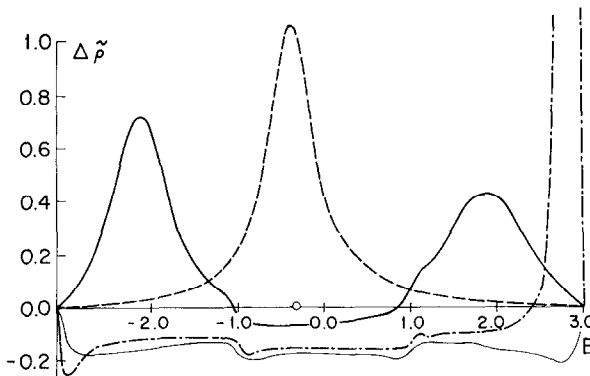

Fig. 1. Total ΔDOS for four adatom–substrate hopping strengths: $V = 0.5$ (dashed), 1.5 (heavy solid), 2.504 (dot-dashed), and 3.5 (light solid). The energy unit is bandwidth/6. The abscissa gives the energy relative to the band center, with the small circle indicating the adatom level $E_a = -0.3$.

with E_a fixed near the center of the band. For weak V $(V = 0.5)$, we see that the delta-function peak at E_a has merely broadened into a Lorentzian, the width of which is proportional to V^2. (Its center is also shifted from E_a by an energy proportional to V^2.) In this regime, it is reasonable to invoke the "virtual level" approximation, which characterizes the level and level shift by energy-independent constants. For a moderately strong potential $(V = 1.5)$, the single peak splits into a lower and an upper peak, corresponding to a bonding and an antibonding resonance, respectively. This double-resonance feature at intermediate-size V is absent in the simpler one-dimensional model discussed by Newns[8]) (whose treatment of the total ΔDOS is otherwise similar to ours) because the real part of his G_{11} (the Hilbert transform of a semi-elliptical DOS) is linear in E within the band. The width of $\Delta\tilde{\rho}$, which relates roughly to the strength of the adatom–surface band, is now characterized by the separation of the two peaks rather than their individual widths; this separation goes more nearly like V than V^2. As V is further increased, the resonances approach their respective band edges and narrow. For V so large that there is a value $E_s^{b(a)}$ below (above) the band such that

$$E_s^{b(a)} - E_a - V^2 \operatorname{Re} G_{11}(E_s^{b(a)}) = 0, \tag{4}$$

we say that a bonding (antibonding) state – which has unit weight – has split off below (above) the band. In fig. 1, we see that for $V = 2.504$, a narrow antibonding resonance exists near the top of the band, while a bonding state has just split off below the band. For $V = 3.5$, the antibonding resonance has also split off above the band and lies at $+3.58$; the bonding state now is at -3.84.

In the strong potential regime, we see that $\Delta\tilde{\rho}$ within the band is relatively insensitive to V. As we can see from eq. (2), within the band it rapidly approaches

$$\pi^{-1} \operatorname{Im}(\partial/\partial E) \ln G_{11}(E), \tag{5}$$

which is negative; the first-order correction is smaller by roughly a factor of V^{-2}. Obviously this negativity is necessary if we are to satisfy the sum rule of eq. (3), since both the bonding and antibonding state have unit weight (i.e. the bonding state will be doubly occupied). Physically, we view atom 1 as separating from the solid and forming a strong covalent bond of energy $2E_s^b$ with the adatom. Indeed, eq. (5) is the expression for (100) cubium with a vacancy at site 1. Since the term surface molecule used in ES and elsewhere[8,9]) has acquired some other connotations[10]), we shall use the name *surface complex* for this regime. A good characterization of the system can be given by allowing the surface complex to rebond to the indented substrate via second-order perturbation theory[11]).

For chemisorption systems we found in ES that V is roughly 1.5 to 2.5. We

fix attention on $V = 1.5$, so that all features of $\Delta\tilde{\rho}$ lie within the band. We now ask how far away from the adatom the perturbation persists. This is easy to investigate since we can naturally decompose the ΔDOS as

$$\Delta\tilde{\rho} = \rho_{aa} + \sum_i \Delta\rho_{ii}, \tag{6}$$

where i ranges over all the substrate sites, and $\Delta\rho_{ii}$ is the local ΔDOS at substrate site i. Using the Dyson's equation method, and noting that the potential V connects only sites a and 1, we find

$$\rho_{aa} = \pi^{-1}\,\mathrm{Im}\,\mathscr{G}_{aa}, \quad \mathscr{G}_{aa} = (E - E_a - V^2 G_{11}(E))^{-1},$$
$$\Delta\rho_{ii} = \pi^{-1}\,\mathrm{Im}\,(T_{11}G_{1i}^2), \quad T_{11} = V^2\mathscr{G}_{aa}, \tag{7}$$

where the script $\mathscr{G}$ denotes the Green's function for the perturbed system, while as before G_{11} and G_{1i} are Green's functions for (100) cubium. In fig. 2 we see that the sum of ρ_{aa} and $\Delta\rho_{11}$ give the double peaked structure of $\Delta\tilde{\rho}$. The comparable peak weights in both curves result from E_a lying near the center of the band; the absence of the trough in ρ_{aa} indicates the omission of $-\delta(E - E_a)$ [cf. eq. (2)]. The absence of the two-peak structure in the nearest and next-nearest surface neighbor ΔDOS curves indicates that the bonding (and antibonding) resonance is highly localized on atoms a and 1, supporting the surface complex picture. We see that convergence site-wise is fairly rapid; however, the rapid decrease in contribution per site is partially compensated by a corresponding increase in number of equivalent sites. We see also that extremes of the nearest and next nearest ΔDOS curves tend to partially cancel each other. Finally, fig. 2 implicitly verifies that the perturbed local DOS, $\Delta\rho_{ii} + \rho_{11}^0$, is non-negative for any surface site i.

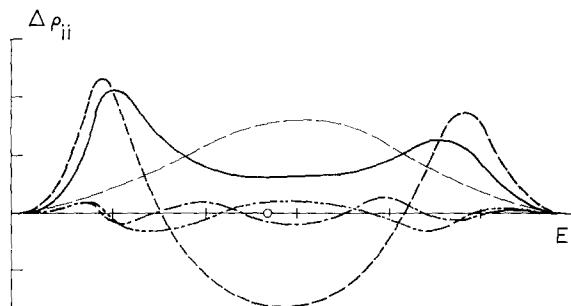(100) cubium is particularly convenient in that the sum over all $\Delta\rho_{ii}$ in the

Fig. 2. Local DOS for the adatom (solid); and the local ΔDOS for the substrate atom directly beneath, called 1 (dashed), and 1's nearest (dot-dot-dashed) and next nearest neighbors (dot-dashed) in the surface plane. The latter two curves are four times the individual site contributions since each has four equivalent sites. E_a is -0.3, V is 1.5, and the scales are identical to fig. 1. Shown in the background (light long dashed curve) is $\rho_{11}{}^0$.

mth layer goes as the imaginary part of the product of T_{11} and a *single* substrate Green's function [7]). As fig. 3 shows, this $\Delta\rho_m$ ($=\Sigma\Delta\rho_{ii}$ in the m th layer) decreases initially fairly rapidly, but remains non-negligible for deeper layers. The existence of rapid and varied wiggles in $\Delta\rho_m$ for the third and fourth layer suggests that surface probes which are sensitive to different depths in the substrate will have similar coarse structure (due to the dominance of the adatom and the top layer) but quite variable fine structure. Additional fine structure, of course, will arise from final state and other effects neglected here; in some cases there may even be additional and variable coarse structure from interference effects.

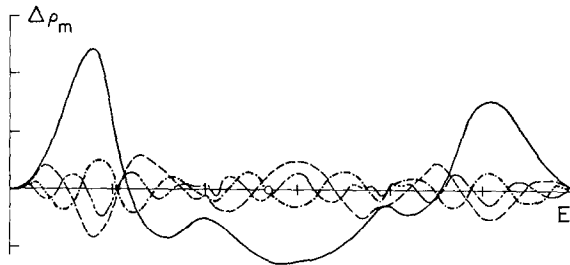To make contact with an experimental system, let us consider photo-

Fig. 3. Planar or subtotal ΔDOS for the top (solid), second (dashed), third (dot-dashed), and fourth (thin solid with double short dashes) layers. The scales are identical to figs. 1 and 2, the adjustable parameters to fig. 2.

emission difference spectra in our simple model, and with the final state being simply plane waves. If we neglect orbital energy effects, then the change in photoelectric yield (ΔPE) due to adsorption is roughly the Fourier transform of $\Delta\rho_{ij}$, or more exactly

$$\Delta\text{PE} \propto \text{Im} \sum_{\mu, \nu} \Delta\mathscr{G}_{\mu\nu}(E_f - \hbar\omega + E_c) \exp(ix_{\mu\nu}), \tag{8}$$

where μ and ν range over both substrate sites i and the adatom a; $\Delta\mathscr{G}$ is the change in the one-electron Green's function (the imaginary part of $\Delta\mathscr{G}$ is $\pi\Delta\rho$), $x_{\mu\nu}$ is $k_f \cdot (R_\mu - R_\nu)$, where R_μ is an atomic site and k_f is the wavevector of the photoemitted electron. The initial energy is the final state energy $(\hbar^2 k_f^2/2m)$ minus the photon energy $\hbar\omega$. E_c is the energy by which the center of the band lies below the vacuum level; it corrects for the fact that the former rather than the latter defines the energy zero.

If we now do an angular average, the phase factor reduces to $x_{\mu\nu}^{-1} \sin x_{\mu\nu}$. For $x_{\mu\nu}$ sufficiently large, this reduces to a Kronecker delta in μ and ν, so that

$$\Delta\text{PE} \propto \text{Im} \sum_\mu \Delta\mathscr{G}_{\mu\mu} = \Delta\rho. \tag{9}$$

Again $\Delta\tilde{\rho}$ should be substituted here since the emission from a free atom is not considered in determining difference spectra. In a real system, say 21.2 eV photons onto tungsten, $x_{\mu\nu}$ is about 9 for nearest neighbors. While the angular factor is thus smaller than unity by an order of magnitude, there is the partially compensating fact that there are several equivalent nearest neighbors. In any case, the Kronecker delta replacement should give a good idea of what the qualitative features of angular averaged ΔPE spectra are. In determining the angular resolved ΔPE spectrum[7]), a process that is more involved than is appropriate to discuss here, we do not need to make the replacement, and so we will have a check of sorts.

Eq. (9) suggests an easy way to consider the effect of damping. We can put in a damping parameter, λ, by hand as follows:

$$\Delta\text{PE} \propto \Delta\tilde{\rho} = \rho_{aa} + \sum_m \Delta\rho_m \rightarrow \rho_{aa} + \sum_{m=1}^{\infty} \Delta\rho_m \exp\left[-\lambda(m-1)\right]. \quad (10)$$

In general such a parameter should be energy and angle dependent, but here we shall treat it as simply a constant. For $\lambda = 0$ we get the total system emission $\Delta\tilde{\rho}$. For $\lambda = \infty$ we see only the surface layer. In fig. 4 we plot these two extremes and the intermediate value of $\lambda = 3/5$. We see that as mentioned above the curves are qualitatively the same, but differ in fine structure. We also plot the contribution of the surface complex, i.e. $\rho_{aa} + \Delta\rho_{11}$, to illustrate that the approximation of using it alone to characterize the adsorption process, as has been done by Gadzuk[12]), is qualitatively not bad at all.

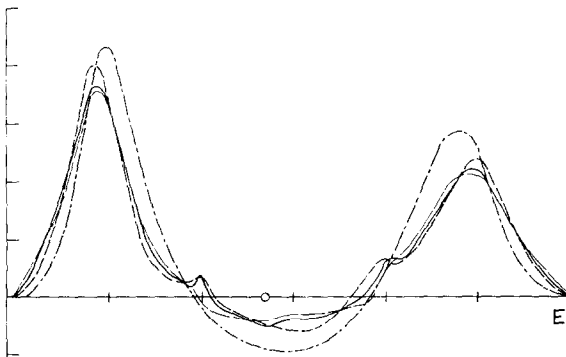Fig. 5 displays actual photoemission difference spectra taken by Plummer

Fig. 4. Damped ΔDOS, suggesting some initial state photoemission effects, as written in eq. (10), with the same scales and adjustable parameters as figs. 2 and 3. The long-dashed curve gives the undamped ΔDOS, while the dashed curve shows the extreme case of emission only from the adatom and top substrate layer. The solid curve pictures a realistic intermediate case with $\lambda = 3/5$. The dash-dot curve indicates the contribution of just the surface complex.

et al.[2]) for various adsorbates on (110) W. Using the prescription $E_a =$ $= -\frac{1}{2}(I + A)$, we find that E_a lies between 6 and 7.5 eV below vacuum level for H, O, and C, while the W band center and width are about -5.5 and 12 eV, respectively[13]). Thus, E_a is placed within $\frac{1}{6}$ bandwidth below the band center, i.e. between -1 and $-\frac{1}{4}$ in the abscissal units of figs. 1 to 4. In making comparisons with previous figures, we note that in photoemission we only
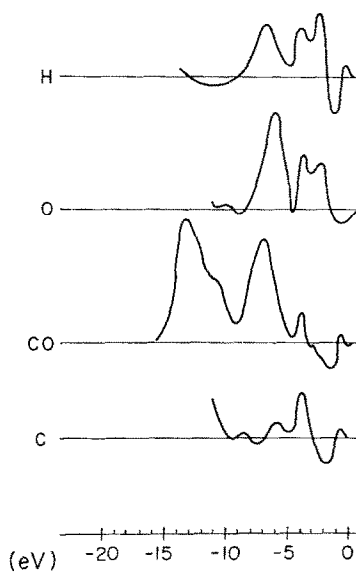

Fig. 5. Photoemission difference spectra in arbitrary intensity units for several adsorbates on the (110) face of tungsten, obtained by Plummer[2]). The depletion region lies about 1 eV below the Fermi level, while the bonding peak is around -6 eV, near the bottom of the band.

see the occupied states of the band. In all cases we see a structure corresponding to moderate to strong binding: a bonding state or resonance near or below the band and a depletion of states in the band region. Clearly any quantitative statement is inappropriate in the present model.

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