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Correlation effects in photoemission from adsorbates: Hydrogen on narrow-band metals

J. Rubio, M. C. Refolio, M. P. López Sancho, and J. M. López Sancho

Instituto de Ciencia de Materiales, Sede A, Consejo Superior de Investigaciones Científicas, Serrano 144, 28006 Madrid, Spain

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This paper deals with photoemission from a one-level atom adsorbed on a metal surface within the context of Anderson's Hamiltonian. The occupied part of the adsorbate density of states (DOS) is calculated by means of a many-electron approach that incorporates the following ingredients: (1) A neat separation between final-state interactions and initial (ground-state) effects. (2) The method (a Lehmann-type representation) leans heavily on the resolvent operator, $R(z)=(z-H)^{-1}$, which is obtained by expressing Dyson's equation in terms of the $(N-1)$-electron states (configurations) that diagonalize the hopping-free part of Anderson's Hamiltonian, thereby including the atomic correlation (U) in a nonperturbative way while expanding in powers of the hopping parameter (V). (3) By using blocking methods, the matrix elements of R are grouped into equivalent 4×4 matrix blocks, with residual interactions, which are then put in correspondence with the sites of a rectangular lattice, thereby making the problem isomorphic to that of finding a *noninteracting* one-electron Green's function in the Wannier representation. (4) Renormalized perturbation theory, along with a series of convolution theorems due to Hugenholtz and Van Hove, allows one to develop a self-consistency equation that automatically takes into account an infinite number of configurations. The resulting DOS is compared with photoemission spectra from hydrogen adsorbed on tungsten (half-filled metal band) and nickel (almost full). Correlation effects turn out to produce peaks at the appropriate energies, so that an unusually good agreement is found despite the featureless, semielliptical DOS adopted for the metal. Only gross features of this quantity, such as width, center, and occupation of the band, seem to matter in a photoemission calculation.

I. INTRODUCTION

The last decade has witnessed an unprecedented growth in our understanding of the electronic properties of adsorbate-covered surfaces. This has been due mainly to the generalized spread of surface spectroscopies as an experimental probe for such systems. Since the connection between experimental spectra and the theoretically calculated densities of states (DOS) is far from trivial, owing to several relaxation effects, a considerable effort has also been made from the theoretical side.[1]

With special reference to photoemission, most theoretical work starts with Anderson's Hamiltonian, usually supplemented by some extra terms specially devised to account for specific relaxation effects.[2] One then tries to calculate the adsorbate one-electron Green's function $G_a(\omega)$ (or the core Green's function, as the case may be) by any of the methods available, such as the equation of motion method with decoupling at some stage, the summation of selected classes of diagrams, etc. Although there is nothing to say in principle against those approaches, they often lead to expressions difficult to interpret in terms of relaxation processes, mainly because the separation of final-state interactions from ground-state effects is, as a rule, difficult within those schemes.

An alternative and recent approach[3,4] is based on the following standard expression for the advanced (or hole) part of the adsorbate Green's function $G_{as}^{<}(E)$:

$$G_{as}^{<}(E)=\left\langle c_a^{\dagger}\frac{1}{E-E_0^N+H-i\eta}c_a\right\rangle$$
$$=-\sum_{i,j}\langle 0\,|\,c_a^{\dagger}\,|\,i\rangle R_{ij}(E_0^N-E+i\eta)\langle j\,|\,c_a\,|\,0\rangle\ , \qquad (1)$$

where $c_a^{\dagger}$ (c_a) is the creation (annihilation) operator for an electron of spin s in the adsorbate level ε_a, $|\,0\rangle$ stands for the ground state of energy E_0^N, and $R_{ij}(z)=\langle i\,|\,(z-H)^{-1}\,|\,j\rangle$ are the matrix elements of the resolvent in a suitable basis set of $(N-1)$-electron states (configurations) which we explain below. Equation (1) is nothing more than the well-known Lehmann representation expressed in this basis set. A first advantage of such an approach lies in the neat separation between final and initial (ground-state) effects it provides: The final-state effects are contained in the R_{ij} while the ground-state effects are given by the coefficients $\langle i\,|\,c_a\,|\,0\rangle$. A second advantage is the straightforward interpretation it provides of the DOS features: the different peaks arise from the poles of R_{ij} and can therefore be assigned to definite configurations of $N-1$ electrons (usually one configuration dominates in each case), which allows following the track to, for example, a relaxation process which may be taking place. A third and final advantage is that $G^{<}$ comes out positive-definite below the ionization threshold, $E_0^{N-1}-E_0^N$, something not necessarily preserved *a priori* when other methods are used. The main disadvantage of this approach is that the calculation of R usually requires a very large basis set, except in the case of an infinitely degenerate impurity level,[5] where the first few configurations give accurate results.[3,4] Another disadvantage is that one must know the ground state in order to find the coefficients $\langle i\,|\,c_a\,|\,0\rangle$.

In this work we shall apply the latter approach to photoemission from a one-level adsorbate (hydrogen) on a one-band metal. For this (spin) doubly degenerate case, one must probably include many configurations to get a reliable result. Although previous calculations[4] show that ground-state energies come out not very far from exact results, when available, the situation is not clear for excited states.[3–5] Therefore, one cannot be satisfied with the first few configurations in a photoemission calculation and, accordingly, the main purpose of this work will be to give a simple and efficient procedure to include a large number of them. Our results will then be compared with those of other work.

II. CHOICE OF THE BASIS SET

We adopt the standard Anderson-Newns Hamiltonian for the one-impurity model, as conventionally applied to chemisorption,[6] which we split as

$$H = H_0 + H' , \tag{2a}$$

where H_0 describes the free (noninteracting) metal-plus-adsorbate system,

$$H_0 = \sum_{k,s} \varepsilon_k n_{ks} + \sum_{s} \varepsilon_a n_{as} + U n_{a\uparrow} n_{a\downarrow} \tag{2b}$$

and H' is the adsorbate-metal mixing term,

$$H' = \sum_{k,s} \frac{V}{\sqrt{\mathcal{N}}} c_{as}^{\dagger} c_{ks} + \text{H.c.} , \tag{2c}$$

which describes hopping of one electron between the adsorbate state $|a_s\rangle$ (of energy ε_a and occupation $n_{as} = c_{as}^{\dagger} c_{as}$) and the $\mathcal{N}$ metal states $|ks\rangle$ (of energy ε_k and occupation $n_{ks} = c_{ks}^{\dagger} c_{ks}$). V is assumed independent of k for the sake of simplicity. U is the intra-adsorbate Coulomb repulsion.

The basis set we adopt for the expansion of (1) is formed by the $(N-1)$-electron states (configurations) which diagonalize H_0. The resolvent will thus be calculated from Dyson's equation

$$R(z) = \frac{1}{z - H_0} + \frac{1}{z - H_0} H' R(z) , \tag{3}$$

or, taking matrix elements between states of the above basis,

$$R_{ij}(z) = \frac{\delta_{ij}}{z - E_i} + \frac{1}{z - E_i} \sum_{l} H'_{il} R_{ij}(z) \tag{4}$$

with $H | i \rangle = E_i | i \rangle$. We expand in H's the hopping part of the Hamiltonian, which mixes different configurations. The adsorbate correlation U is treated nonperturbatively from the start. Indeed, the doubly occupied configurations, with two electrons in the adsorbate, feel the full effect of U, which appears in the corresponding matrix elements of the diagonal operator $(z - H_0)^{-1}$. The importance of this choice of basis to expand $R(z)$ cannot be overemphasized. Any expansion which implies, directly or indirectly, doing perturbation theory in U fails to account for, e.g., the Kondo peak in the photoemission spectrum.[7]

III. TRANSFORMATION TO A RECTANGULAR LATTICE

Solving (4) iteratively in a naive way, i.e., putting repeatedly just $R_{ij}(z) = \delta_{ij}/(z - E_i)$ on the right-hand side, gives the standard Born series which, usually, converges very slowly. In other words, one has to invert a very large $(z-H)_{ij}$ matrix to get a reliable result for R. We now develop a method which avoids inverting large matrices.

For this purpose it is best to represent graphically the pattern of configurations generated by the Hamiltonian. Let us start with the state

$$|P_0\rangle = \prod_{k,s\ (\text{occ})} c_{ks}^{\dagger} |\text{vac}\rangle \tag{5}$$

with the adsorbate level empty and the metal filled up to the Fermi level, $E_F = 0$. In this state the adsorbate is positively charged, i.e., *one* electron has been *removed* from it and, consequently, is denoted by P_0. It is the fundamental building block in our photoemission calculation. Applying now $z - H$ one gets

$$\begin{aligned}(z - H_0) | P_0 \rangle &= \frac{V}{\sqrt{\mathcal{N}}} \sum_{k\ (<k_F),s} c_{as}^{\dagger} c_{ks} | P_0 \rangle \\ &= V_1 \sum_{s} | A_{0s} \rangle ,\end{aligned} \tag{6}$$

where $|A_{0s}\rangle$ are the normalized states

$$| A_{0s} \rangle = \frac{1}{(N_1)^{1/2}} \sum_{k\ (<k_F)} c_{as}^{\dagger} c_{ks} | P_0 \rangle \tag{7}$$

(N_1 is the number of occupied k states) where one electron of spin s has jumped from the metal to the adsorbate. These states are neutral from the adsorbate standpoint. In the derivation of (6) we have taken $E_0 = \sum_{k\ (<k_F)} \varepsilon_k$ as the reference energy and have written $V_1 = (N_1/\mathcal{N})^{1/2} V$, i.e., V_1 appears scaled by the occupied fraction of the band. This is only natural since only electrons from occupied states can jump into the adsorbate.

Acting with $z - H$ on the states $|A_{0s}\rangle$, a second electron can be transferred to the adsorbate, leading to the state

$$\begin{aligned}| N_{0s\bar{s}} \rangle &= \frac{1}{(N_1)^{1/2}} \sum_{k'\ (<k_F)} c_{a\bar{s}}^{\dagger} c_{k'\bar{s}} | A_{0s} \rangle \\ &= \frac{1}{N_1} \sum_{k,k'\ (<k_F)} c_{as}^{\dagger} c_{a\bar{s}}^{\dagger} c_{k'\bar{s}} c_{ks} | P_0 \rangle \\ &= | N_{0\bar{s}s} \rangle \equiv | N_0 \rangle \quad (\text{independent of } s)\end{aligned} \tag{8}$$

with two electrons in the adsorbate (negatively charged) and two holes in the metal. Likewise, the adsorbate electron can jump to the metal leading to new states (N_2 is the number of empty k states)

$$\begin{aligned}| P_{1s} \rangle &= \frac{1}{(N_2)^{1/2}} \sum_{k'\ (>k_F)} c_{k's}^{\dagger} c_{as} | A_{0s} \rangle \\ &= \frac{1}{(N_1 N_2)^{1/2}} \sum_{\substack{k\ (<k_F) \\ k'\ (>k_F)}} c_{k's}^{\dagger} c_{ks} | P_0 \rangle ,\end{aligned} \tag{9}$$

where the adsorbate is again ionized and one electron-hole pair has been formed. These states we call, therefore, P_{1s}, i.e., positively charged states with one electron-hole pair of spin s. It is not difficult to derive the following equation relating the states (7)–(9):

$$(z-H_0)\,|A_{0s}\rangle = V_1\,|P_0\rangle + V_1\,|N_0\rangle + V_2\,|P_{1s}\rangle\ , \tag{10}$$

where $V_2=(N_2/\mathcal{N})^{1/2}V$, i.e., V appears in front of $|P_{1s}\rangle$ scaled by the unoccupied fraction of the band. This is physically clear since, in this process, the adsorbate electron is allowed to jump into empty metal states only.

Repeated applications of $z-H$ introduce new configurations, with an increasing number of electron-hole pairs, leading to an infinite sequence of equations which can be represented by the network of sites and bonds shown in Fig. 1. The sites in this figure are in correspondence with the different configurations, and the bonds, of two kinds, correspond to V_1 and V_2. Thus, P_0, A_0 (two sites), and N_0 represent the states with the same labels, (5), (7), and (8), respectively. For simplicity in the labeling of the figure, we have not written explicitly $A_{0\uparrow}$ and $A_{0\downarrow}$ as no confusion should arise. Similarly, the sites labeled P_n, A_n, and N_n denote configurations where n electron-hole pairs have been added to P_0, A_0, and N_0. Since the addition of n electron-hole pairs to a given configuration gives rise to $n+1$ possible configurations, P_n and N_n appear $n+1$ times in the figure while A_n appears $2(n+1)$ times. Figure 1 must be interpreted as follows: when H acts on P_0, this state is coupled with both A_0's through the hopping interaction V_1 (first-order calculation, equivalent to first-order Brillouin-Wigner perturbation theory). A second application of H couples the two states A_0 with the new states N_0 (through V_1) and P_1 (through V_2), etc. Each new application of the Hamiltonian takes us to the next diagonal, so that, e.g., after five applications of H, we reach the diagonal formed by the sites labeled A_2.

A method based on the above scheme has been applied elsewhere[8] to electron-loss spectroscopy of hydrogen adsorbed on metals. Here we shall handle Fig. 1 somewhat differently and shall thereby develop a new summation scheme which is both more transparent and converges more quickly. Notice simply that the square formed by P_0, A_0, N_0, and A_0 (labeled "0" in Fig. 2), can be taken as a unit cell of a rectangular lattice with a corner (the zeroth site), provided we ignore that different cells correspond to configurations with a different number of electron-hole pairs. The effective interactions between blocks are the 4×4 matrices

$$\mathcal{V}=\begin{bmatrix}0&0&0&0\\V_2&0&0&0\\0&0&0&V_2\\0&0&0&0\end{bmatrix}$$

and (11)

$$\mathcal{V}'=\begin{bmatrix}0&0&0&0\\0&0&0&0\\0&V_2&0&0\\V_2&0&0&0\end{bmatrix}$$

By this blocking device, the problem of calculating the matrix elements of the resolvent becomes isomorphic with that of calculating the matrix elements of a *noninteracting* one-electron Green function for a rectangular lattice in the Wannier representation (again ignoring the electron-hole pairs). This isomorphism does not apply to

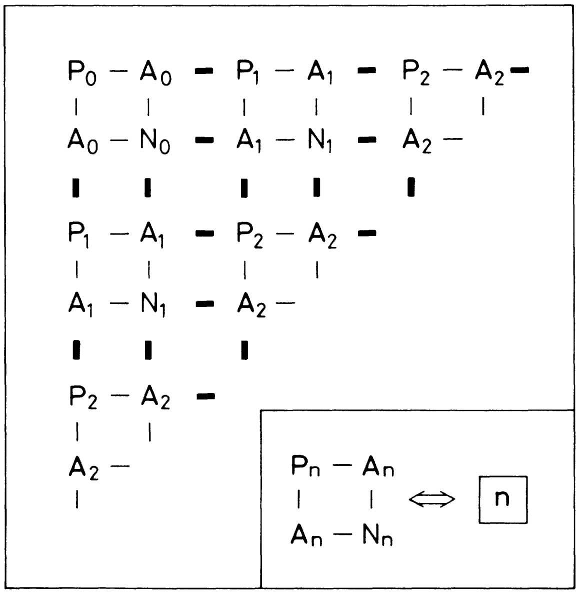

FIG. 1. Network of sites and bonds representing the configuration pattern generated by repeated application of Anderson's Hamiltonian to the ionic configuration $|P_0\rangle$. Light and heavy bonds represent V_1 and V_2.

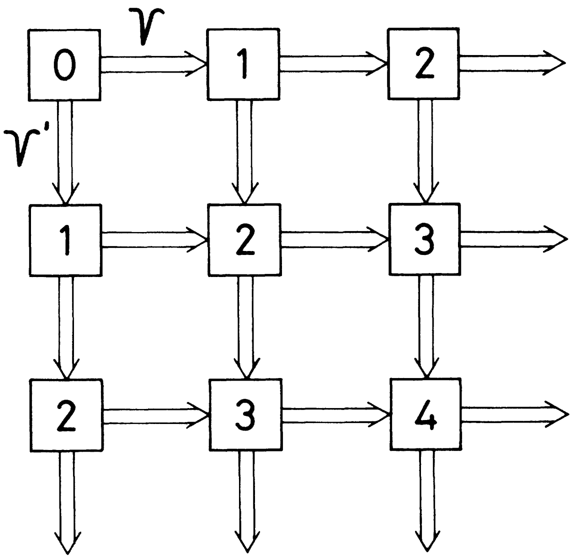

FIG. 2. Rectangular lattice obtained after condensing the sites of Fig. 1 into blocks of four configurations $(P_n, A_{n\uparrow}, A_{n\downarrow}, N_n)\rightarrow n$. Only the index n, indicating the number of electron-hole pairs, survives. $\mathcal{V}$ and $\mathcal{V}'$ are the effective interactions for adding spin-up and spin-down electron-hole pairs, respectively.

Fig. 1. because, there, one has three kinds of sites according to the adsorbate occupancy (P, A, N), so that an altogether different scheme is required.[8]

IV. REDUCTION TO THE ZEROTH CELL: SELF-CONSISTENT SUMMATION OF ELECTRON-HOLE PAIRS

Now we deal with the difficulty posed by the electron-hole pairs. For that purpose, consider one of the squares labeled "1" in Fig. 2. If we cut its back bonds, this square marks the beginning of a new rectangular lattice which differs from the initial one by the consistent addition of one electron-hole pair. Let R_{00} be the 4×4 resolvent matrix associated with the top-left square, i.e., the matrix formed by the R_{ij} among the first four configurations (the zeroth cell), and let R'_{11} denote the 4×4 matrix associated with the indented square (without backbonds) just described. Then, according to a theorem of Hugenholtz and Van Hove,[9] R'_{11} must be the convolution of R_{00} with the electron-hole–pair Green function, that is,

$$R'_{11}=R_{00}\otimes G_{eh}$$

and, in general,

$$R'_{nn}=R_{n-1,n-1}\otimes G_{eh}\ , \tag{12}$$

where

$$G_{eh}(z)=\frac{1}{N_1N_2}\sum_{\substack{k\,(<k_F)\\ k'\,(>k_F)}}\frac{1}{z-(\varepsilon_{k'}-\varepsilon_k)}\ .$$

This set of recurrence relations, Eqs. (12), strongly simplifies the evaluation of R since it allows expressing any matrix element in terms of the matrix elements in the zeroth cell (R_{00}). In particular, Eqs. (12), in connection with renormalized perturbation theory arguments,[10] lead directly to a self-consistency equation for R_{00}. Indeed this quantity is given by

$$\frac{1}{R_{00}}=(z-H)_{00}-\Sigma_{00}(z)\ , \tag{13}$$

where $(z-H)_{00}$ is the $z-H$ matrix in the zeroth cell and Σ_{00} is the zeroth cell self-energy, given by the sum over self-avoiding paths[10]

$$\begin{aligned}\Sigma_{00}(z)=&\,\mathcal{V}R'_{11}\mathcal{V}^{\dagger}+\mathcal{V}'R'_{11}\mathcal{V}'^{\dagger}+\mathcal{V}R'_{11}\mathcal{V}'R'_{22}\mathcal{V}^{\dagger}R'_{11}\mathcal{V}'^{\dagger}\\ &+\mathcal{V}'R'_{11}\mathcal{V}R'_{22}\mathcal{V}'^{\dagger}R'_{11}\mathcal{V}^{\dagger}+\cdots\ ,\end{aligned} \tag{14}$$

in terms of the indented (backbonds and upward bonds cut) R'_{11}.

Equations (12)–(14) give a self-consistency equation for R_{00}, namely,

$$\begin{aligned}\frac{1}{R_{00}}=&\,(z-H)_{00}-\mathcal{V}R_{00}\otimes G_{eh}\mathcal{V}^{\dagger}-\mathcal{V}'R_{00}\otimes G_{eh}\mathcal{V}'^{\dagger}\\ &-\mathcal{V}R_{00}\otimes G_{eh}\mathcal{V}'R_{00}\otimes G_{eh}\otimes G_{eh}\mathcal{V}^{\dagger}R_{00}\otimes G_{eh}\mathcal{V}'^{\dagger}\\ &-\mathcal{V}'R_{00}\otimes G_{eh}\mathcal{V}R_{00}\otimes G_{eh}\otimes G_{eh}\mathcal{V}'^{\dagger}R_{00}\otimes G_{eh}\mathcal{V}^{\dagger}\\ &-\cdots\ ,\end{aligned} \tag{15}$$

where we have eliminated all reference to R_{ij}'s outside the zeroth cell. Equation (15) can be solved by iteration starting from $R_{00}=0$. The procedure is to be carried on until self-consistency is achieved within a given accuracy. Since each new iteration introduces a set of configurations with one additional electron-hole pair, the number of iterations required to achieve self-consistency tells us the number of electron-hole pairs contained in the last set of configurations retained within that accuracy. Once R_{00} is known, the rest of the R_{ij} can be readily obtained by means of a set of recurrence relations easily derived from Eq. (4). Now we have to find the ground state, $|0\rangle=\sum_{\mu}c_{\mu}\,|\mu\rangle$ in terms of some N-electron basis set. The coefficients c_{μ} are found trivially from the first column of the matrix $R_{\mu\nu}$, evaluated at the maximum of lowest energy. The required matrix elements are obtained by a calculation similar to the one described above, but starting from the state $c_a^{\dagger}\,|P_0\rangle$.

V. THE RESOLVENT SPECTRAL DENSITY: FINAL STATES

In the application of the method, we have taken a metal described by a half-occupied semielliptical DOS with a bandwidth of 8 eV, intended to mimic metals halfway across a transition series. The adsorbate ionization level (-13.6 eV) and affinity level (-0.7 eV), appropriate for hydrogen, were corrected by an image potential of 4 eV (with a net intra-adsorbate repulsion of 4.9 eV).[11] The hopping strength V was adjusted to give a chemisorption energy of 3 eV when calculating the ground-state energy. Figure 3 shows the resolvent DOS, $A(E)=(1/\pi)\mathrm{Im}\sum_i R_{ii}(E_0-E+i\eta)$, for (a) the first block of four configurations (zeroth cell) and (b) after iterating Eq. (15) to self-consistency. At first sight, both curves look rather dissimilar but, upon closer inspection. Figure 3(a) is not unreasonable as far as the energy locations of the peaks are concerned. There are two main differences: first the appearance of a sharp, almost deltalike, peak of the Kondo type at the Fermi level and, second, the line-shape structure in Fig. 3(b) is almost absent in Fig. 3(a). Most of the strength of the two deltalike peaks in Fig. 3(a) is distributed along the whole spectrum of Fig. 3(b) with an accompanying small shift in peak locations. A broad shoulder on the high-energy side of the spectrum, at about 15 eV below the Fermi level, is also noticeable.

All these new features, not present in Fig. 3(a), suggest that the self-consistent solution just presented seems essential if one is to discuss line-shape or lifetime effects. As is well known, these effects are most relevant for the understanding of several electron- and photon-induced processes as, e.g., electron- and photon-stimulated desorption (ESD and PSD) as well as many Auger-induced processes where long-lived complex excitations of two or more holes seem to play the dominant role in desorption and/or dissociation.[12,13]

The resolvent spectral density is just the density of final states (DOFS), without any reference to the ground state in which the system was *before* being excited. It contains valuable information about the many-body interactions among the $(N-1)$-electron states into which the system can evolve after the excitation. However, the interesting quantity from the experimental point of view is the projected DOS to which we now turn.

VI. THE ADSORBATE DOS: COMPARISON WITH PHOTOEMISSION SPECTRA

Figure 4(a) shows the occupied part of the adsorbate DOS $(E_F=0)$, $n(E)=(1/\pi)\mathrm{Im}G_a^<(E)$, which is just the projection of $A(E)$, Fig. 3(b), onto the ground state [cf. Eq. (1)]. This projection gives rise to a drastic rearrangement in peak heights (Fig. 4 has been amplified by a factor of 5) which represents the ground-state effect. $n(E)$ and not $A(E)$ is to be compared with the experimental spectra. Figure 4(b) gives $n(E)$ for a similar calculation with a metal DOS of 4 eV bandwidth and 0.9 occupancy, intended to mimic metals at the end of the transition series, Ni, Pd, or Pt. It is remarkable that, by simply adjusting the bandwidth and the position of the Fermi level (rather the band center, since $E_F=0$) we are able to produce DOS of such a different shape as Figs. 4(a) and 4(b). Moreover, a preliminary attempt to compare with experimental results[14,15] shows that the structures of Figs. 4(a) and 4(b) go in the right direction, reproducing qualitatively, and even semiquantitatively, the experimental trends. Thus, Fig. 4(a), intended for metals halfway along the transition series, shows (besides the sharp peak at the Fermi level and some features on the high-energy side of the spectrum which we leave for the end) a main peak at -4.5 eV, surrounded by a lower peak at -2.5 eV and a shoulder at -6.5 eV. This structure correlates quite nicely with the experimental spectrum given by Blanchet *et al.*[14] for normal photoemission from H on W(110)

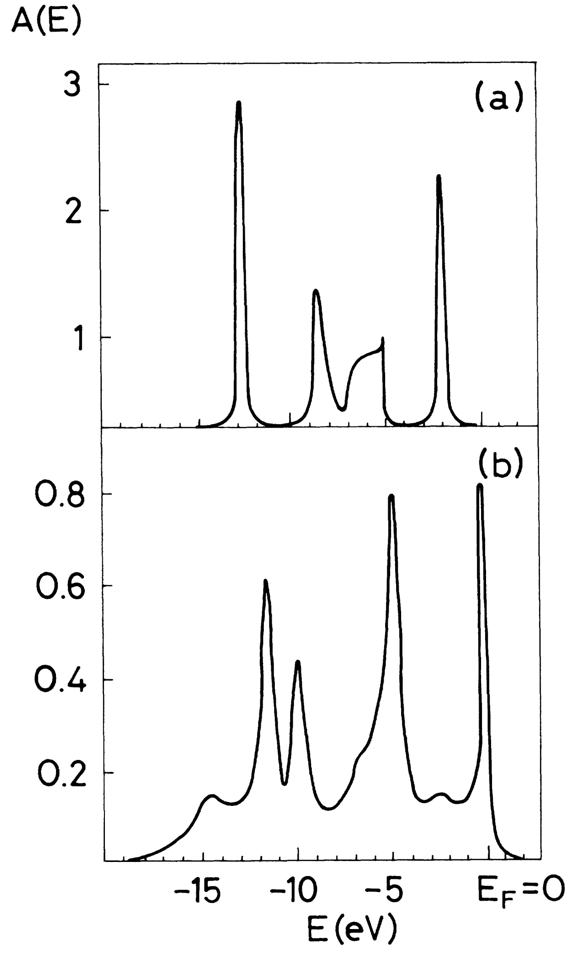

FIG. 3. Resolvent spectral density, $A(E)$, or density of final states. (a) For the zeroth cell. (b) After iterating Eq. (15) to self-consistency.

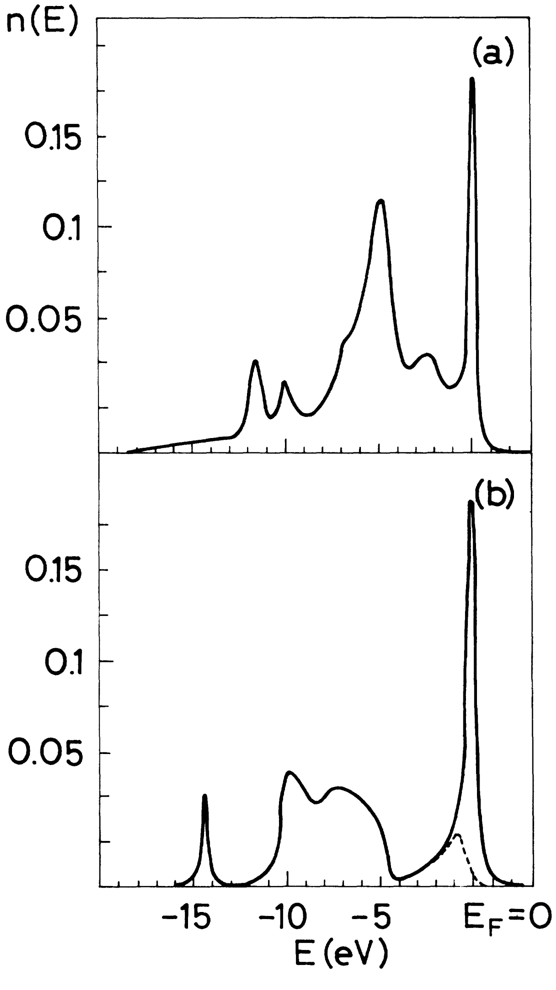

FIG. 4. Adsorbate density of states (DOS) for hydrogen adsorbed on (a) a half-occupied semielliptical DOS of 8 eV bandwidth and (b) a 0.9 occupied semielliptical DOS of 4 eV bandwidth. Adsorbate parameters are (in eV) $a=-8.6$ (with respect to $E_F=0$), $U=12.9$, image potential $V_{\mathrm{im}}=4$.

with 50-eV photons [Fig. 1(b) of this reference], which shows just the same structure, but displaced by 1 eV towards the Fermi level. This is not surprising since we have taken a work function of 5 eV in all cases. Figure 4(b), in contrast, shows a broad structure, centered at about -2 eV, superimposed on the deltalike peak at the Fermi level plus two broad features at -7 and -10 eV, features which also correlate nicely with the photoemission spectrum at the Γ point found by Greuter *et al.*[15] for H on Ni(111) with 40-eV photons.

VII. COMPARISON WITH OTHER WORK AND CONCLUDING REMARKS

Turning now to other theoretical work, the general structure of Fig. 4(a) is in good qualitative agreement with the DOS calculated by Stollhoff[16] for H on jellium. He used the equation-of-motion method supplemented by a separate evaluation, via configuration mixing, of some static correlation functions. The main difference with respect to our $n(E)$ lies in the Fermi-level peak, quite pronounced in our case, in contrast to the rather incipient one found by Stollholff. Finally, Figs. 4(a) and 4(b), like Stollhoff's $n(E)$, also show a high-energy structure beyond -10 eV which probably can be correlated with ESD processes. This aspect is being presently analyzed in detail and will be the subject of a future publication.

It is most intriguing that a calculation based on configuration interaction between a localized level and such a simple metal DOS as that adopted here can reproduce the salient features of photoemission spectra. The interplay among different configurations seems to conspire to produce peaks at the appropriate energies in the final result $n(E)$. The heights and line shapes of these peaks are, furthermore, in reasonable agreement with experiment; this cannot be said of the spectral density of final states, $A(E)$. This quantity presents peaks at the right energies (as well as some other peaks and shoulders in many cases) but with shapes and heights quite at odds with experimental spectra. It is just the process of averaging over the ground state which makes the right peaks survive with the right shape and height.

From this work, one is tempted to conclude that the detailed form of the metal DOS is unimportant in a photoemission calculation. Only gross features such as the bandwidth, center of energy, and position of the Fermi level seem to matter. This situation is familiar in the calculation of other quantities like, e.g., the chemisorption energy,[17] but not in electron spectroscopies. It would be most helpful in this connection to see calculations similar to the one presented here using realistic metal DOS. One could then learn something about the relative contribution of electron correlation and metal orbitals to photoemission spectra from simple adsorption systems.

ACKNOWLEDGMENT

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[1] *Many-Body Phenomena at Surfaces,* edited by D. Langreth and H. Suhl (Academic, New York, 1984), Chap. III, and references therein.

[2] For a good review, see B. Gumhalter, Prog. Surf. Sci. **15**, 1 (1984).

[3] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

[4] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **31**, 4815 (1985).

[5] T. V. Ramakrishnan, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. P. Maple (North-Holland, Amsterdam, 1981), p. 13; T. V. Ramakrishnan and K. Sur, Phys. Rev. B **26**, 1798 (1982); P. W. Anderson, in *Valence Fluctuations in Solids,* p. 451.

[6] D. M. Newns, Phys. Rev. **178**, 1123 (1969).

[7] N. R. Krishna-murthy, J. W.. Wilkins, and K. G. Wilson, Phys. Rev. B **21**, 1003 (1980); **21**, 1044 (1980).

[8] J. Rubio, J. M. Lopez Sancho, M. C. Refolio, and M. P. Lopez Sancho, Surf. Sci. **199**, 297 (1988).

[9] N. M. Hugenholtz, Physica **23**, 481 (1957); N. M. Hugenholtz and van Hove, *ibid.* **24**, 363 (1958).

[10] E. Feenberg, Phys. Rev. **74**, 206 (1948); K. M. Watson, *ibid.* **105**, 1388 (1957); P. W. Anderson, *ibid.* **109**, 1492 (1958).

[11] A screened value for U of some 5–6 eV seems quite reasonable at the metal-hydrogen equilibrium distance (≈ 1 Å). We could equally well take an image potential between, say, 3 and 5 eV without the final numbers changing too much.

[12] D. E. Ramaker, in *Desorption Induced by Electronic Transitions–DIET II,* Vol. 4 of *Springer Series in Surface Sciences,* edited by W. Brenig and D. Menzel (Springer-Verlag, Heidelberg, 1985), p. 10.

[13] D. R. Jennison, E. B. Sechel, and J. A. Kelber, in *Desorption Induced by Electronic Transitions–DIET II,* Ref. 12, p. 24.

[14] G. B. Blanchet, N. I. Dinardo, and E. W. Plummer, Surf. Sci. **118**, 496 (1982).

[15] F. Greuter, I. Strathy, and E. W. Plummer, Phys. Rev. B **33**, 736 (1986).

[16] G. Stollhoff, Surf. Sci. **128**, 383 (1983).

[17] R. Haydock and A. J. Wilson, Surf. Sci. **82**, 425 (1979); C. M. Varma and A. J. Wilson, Phys. Rev. B **22**, 3795 (1980); A. J. Wilson and C. M. Varma *ibid.* **22**, 3805 (1980).