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Effect of surface charge fluctuations on the spectral density of chemisorbed atoms

H. Kranz*
Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

A. Griffin
Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada

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Basing our analysis on the Anderson-Newns model for H chemisorption, we develop a systematic method of calculating the adatom self-energy arising from the effect of substrate charge fluctuations. Using the method of functional derivatives, we generate a Dyson equation for the adatom Green's function and evaluate the self-energies due to the hopping and Coulomb interactions between metal and atom to second order. The latter involves the substrate density response function, and this allows us to include the effect of surface plasmons, bulk plasmons, and the particle-hole continuum of the metal surface on an equal footing. The latter become increasingly important close to the surface, where simple image-potential arguments are no longer adequate. We formulate our theory treating the adatom Coulomb repulsion U perturbatively (Newns, Hertz and Handler) as well as in the atomic limit (Brenig and Schönhammer, Bell and Madhukar). Keeping only surface plasmons, we discuss the relaxation shifts and surface-plasmon satellites of the H-atom spectral density within the context of the Brenig-Schönhammer approximation. In particular, we show how the effective Coulomb repulsion U is reduced to $U-2V_I$. We also prove that the substrate-induced self-energy term which gives rise to the above changes on the spectral density has no effect on the net chemisorption energy. The small image-potential energy shift of the main resonance is canceled by the large shift associated with the weak surface-plasmon satellite. Much of our theoretical analysis is applicable to the core-level spectrum, and not just the valence electrons involved in chemisorption.

I. INTRODUCTION

Considerable progress has been made in recent years in the theoretical understanding of chemisorption on metal surfaces, using a variety of approaches (see Ref. 1). In the present paper, we shall be concerned with the effect that collective charge fluctuations in the substrate have on the electronic density of states $N(\omega)$ of chemisorbed atoms. Basing our calculations on the well-known Anderson-Newns Hamiltonian,[2,3] we develop a systematic way of dealing with substrate charge fluctuations which are coupled to the adatom electron density via the Coulomb interaction (K). To second order in K, the adatom self-energy is given directly in terms of the substrate density response function χ^n, and thus surface plasmons, bulk plasmons, and particle-hole modes of the metal substrate enter on an equal footing.

Our systematic approach avoids the somewhat *ad hoc* manner in which surface plasmons are often introduced in discussions of the electronic states of adsorbed atoms.[4] Our general self-energy expressions can be used when either the adatom Green's function $G_{aa}(\omega)$ or the substrate density response function $\chi^n(\omega)$ have a complicated frequency dependence. If we consider the simple case when both exhibit sharp resonances, our results lead to the usual relaxation shifts and surface-plasmon satellites exhibited by the adatom spectral density $N(\omega)$. We shall develop our theory with the specific example of H chemisorbed on a transition-metal surface in mind. However the formalism is obviously applicable with minor changes to the problem of the core-level structure of chemisorbed and physisorbed atoms, as studied by x-ray photoemission spectroscopy (XPS). This has been an area of very active research in recent years (see, for example, Refs. 4 and 5). In addition, while in applications we shall mainly concentrate on the case for which there is no significant charge transfer between metal and adatom, our general formalism allows such effects to be considered in a self-consistent manner. In a related topic, we note that recent work[6-8] has emphasized the importance of treating the changes in the valence electronic states due to charge transfer which results from exciting a core electron in x-ray photoemission experiments.

The Anderson-Newns parametrization[3] of the chemisorption of hydrogen includes the Coulomb interactions (U) between two electrons of opposite spin in the 1s state of the adatom and a hopping interaction (V) which allows the transfer of electrons between the adatom and the metal substrate. We augment this model to include the Coulomb interaction (v) between metal electrons (this will give rise to plasmon modes) and the Coulomb interaction (denoted by K) between metal and adatom charge densities. The first part of our program is to develop equations of motion for the adatom self-energy using the functional derivative technique.[9] We then evaluate the self-energy to second order in the Coulomb interaction K. This involves the density response function of the substrate and the adatom Green's function. The hopping self-energy is given to second order in V, and involves the substrate electron Green's function. The adatom Coulomb repulsion is treated perturbatively[2] in Sec. II (appropriate to case $V \gg U$) and exactly[10] (appropriate to the atomic limit $U \gg V$) in Sec. III.

In order to evaluate the self-energies obtained in Secs. II and III, we must decide on some model for the substrate. In dealing with the transition metals, it has often been assumed that the hopping interaction V mainly involves the narrow d-band electrons. While this seems to be the case[11,12] with H on Pt and Pd, there is some evidence that the broad sp band is just as important as the d band when dealing with H on Ni.[11,13] In our numerical calculations, we have simply used the semielliptical model for the substrate Green's function involved in the hopping self-energy. In the present paper, our main interest is in the effect of the Coulomb interaction K, in conjunction with some nontrivial approximation for the hopping self-energy. Similar calculations may be carried out with more realistic hopping self-energies as appropriate to studies of specific metal surfaces. In this connection, we note that Schönhammer and Gunnarsson[13,14] have had some success with the use of semielliptical models for both the narrow d band and the wide sp band.

As we have indicated above, the effect of the Coulomb interaction K is to couple the adatom electrons into the density response function of the metal substrate. In Sec. IV, we assume this coupling is mainly to the s electrons and use the semiclassical infinite barrier model in conjunction with the random-phase approximation (RPA). This model has been extensively studied in recent years in a variety of surface problems (see, for example, Refs. 15-17). It has previously been used by Gadzuk[4] as well as Newns and coworkers[18,19] in computing the relaxation shift of core electron states. If we also use a local approximation for the bulk dielectric function of the metal, then our expression for the self-energy to second order in K is identical to what we would have obtained if the substrate was treated as a Bose gas of dispersionless surface plasmons. In this limit (which is not really adequate when the adatom is very close to the surface as in chemisorption), Hewson and Newns[20] have discussed the image potential shifts and surface plasmon satellites of an adatom with a *single* broadened level.

In Sec. V, we examine the effect of the surface plasmons on the adatom spectral density given by the Brenig-Schönhammer approximation[10] as derived in Sec. III. In this atomic limit, the adatom Green's function may exhibit up to four peaks and each is found to exhibit characteristic image-potential shifts and surface-plasmon satellites. However, in Sec. VI, we prove that the total chemisorption energy is uneffected by all these spectral-density changes as long as there is no net charge transfer. This is an illustration of Lundqvist's "zero-work" or compensation theorem,[21,5] first studied in connection with the effect of charge fluctuations on the bulk binding energy of core electrons.

In transition metals, the charge fluctuation spectrum is in fact still not very well understood, whether in bulk or systems with a surface. There is considerable indication that band-structure effects are quite important in understanding bulk and surface plasmons in transition metals.[22] Moreover the surface plasmons resonances are quite broad (width of several eV). The advantage of our general formulation is that we can easily work with more realistic models of the density response function when they become available in the future.

In concluding this introduction, we remark that we have also carried out an analogous study[23,24] of the effect of substrate d-band spin fluctuations on chemisorbed atoms, with emphasis on the critical effects which occur near the ferromagnetic transition temperature. Much of the theory is formally very similar to that given in Secs. II–IV. Some of the notation in this paper has been chosen with this generalization in mind.

II. ADSORBATE GREEN'S FUNCTION VIA FUNCTIONAL DERIVATIVES: HARTREE-FOCK

To begin with, let us write down the model Hamiltonian we shall base our analysis on. For our purposes, the adatom can be described by[2,3]

$$H_a = \sum_\sigma \epsilon_a \hat{c}^\dagger_{a\sigma}\hat{c}_{a\sigma} + \frac{U}{2}\sum_\sigma \hat{n}_{a\sigma}\hat{n}_{a,-\sigma}, \tag{2.1}$$

where $\hat{c}^\dagger_{a\sigma}$ and $\hat{c}_{a\sigma}$ are the creation and annihilation operators of an adatom electron in state a with energy ϵ_a and with spin σ (we limit ourselves to a single valence level). It will be convenient to describe the metal electrons in a site representation

$$H_m = \sum_{ij\sigma} T_{ij}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \sum_{ij} v_{ij}\hat{n}_i\hat{n}_j . \tag{2.2}$$

Here T_{ij} is the appropriate hopping matrix element, $\hat{c}^\dagger_{i\sigma}$ is the creation operator for an electron in a localized state labeled by i and spin σ. The Coulomb interaction v between the metal electrons is represented by the last term in (2.2), with

$$n_i = \sum_{\sigma} n_{i\sigma}, \quad n_{i\sigma} \equiv \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}. \tag{2.3}$$

Finally, the adatom is coupled to the metal electrons through the hopping interaction and the Coulomb interaction

$$H_{ma} = \sum_{i,\sigma} (V_{ai}\hat{c}^{\dagger}_{a\sigma}\hat{c}_{i\sigma} + V_{ia}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{a\sigma}) + \sum_{i} K_{ai}\hat{n}_i(\hat{n}_a - 1), \tag{2.4}$$

where the -1 takes into account the (+) charge on the adatom nucleus.

The electronic state label i includes both site position and band index. It is convenient in formal Green's-function calculations not to differentiate between the s and d electrons. However, at the final stage, we can take into account that usually (a) it is the mobile s and sp-band electrons in the metal which dominate the charge fluctuation spectrum of the metal and also are most important in coupling (screening) to the adatom. That is, the interactions v_{ij} and K_{ai} are only considered for the wide-band s and p electrons. (b) Only the d-electron wave functions overlap strongly on to adatom and thus the hopping interaction V_{ai} is generally only kept for the (narrow-band) d-electrons (see, however, Refs. 11–13).

In the usual discussions of chemisorption, the Coulomb interactions (v and K) are ignored. With their inclusion, the adatom can couple directly (via K) into the plasmon oscillations (which arise as a result of v) involving the conduction electrons of the substrate.

Our aim is to find the spectral density of the adatom Green's function. We shall do this by taking functional derivatives with respect to auxiliary fields.[9] We derive formally exact equations which can be iterated to give a systematic expansion for the adatom self-energy. However we shall only use it to find the self-energy to second order in V, U, and K. In the absence of the Coulomb coupling K, our results are identical to those obtained by Newns[2] appropriate to $V \gg U$. In Sec. III, we shall treat the hopping interaction V using the Brenig-Schönhammer approximation[10] ($U \gg V$).

Following Kadanoff and Baym,[9] we define thermal Green's functions in the standard way[25]:

$$G^{\sigma}_{rs}(\tau,\tau') \equiv -i\frac{\langle T[\hat{S}\hat{c}_{r\sigma}(\tau)\hat{c}^{\dagger}_{s\sigma}(\tau')]\rangle}{\langle T(\hat{S})\rangle} \equiv \langle\langle \hat{c}_{r\sigma}(\tau)\hat{c}^{\dagger}_{s\sigma}(\tau')\rangle\rangle. \tag{2.5}$$

Here and elsewhere, r and s include metal states (i, j) as well as the orbital state (a) of the adatom, σ and σ' represent the spin label, T is the usual time-ordering operator (largest times to the left), and the times are restricted to the domain $0 \leqslant \tau$, $\tau' \leqslant -i\beta$ (we set $\hbar = 1$). The operator $\hat{S}$ contains the auxiliary external scalar fields

$$\hat{S} \equiv \exp\left(-i\int_0^{-i\beta} d\tau \sum_{r\sigma} X^{\sigma}_{r}(\tau)\hat{c}^{\dagger}_{r\sigma}(\tau^{\dagger})\hat{c}_{r\sigma}(\tau)\right). \tag{2.6}$$

The functional derivatives with respect to $X^{\sigma}_{r}(\tau)$ are given by

$$\delta G^{\sigma}_{rs}(\tau,\tau')/\delta X^{\sigma_1}_{r_1}(\tau_1) = -i\langle\langle \hat{c}^{\dagger}_{r_1\sigma_1}(\tau_1^{\dagger})\hat{c}_{r_1\sigma_1}(\tau_1)\hat{c}_{r\sigma}(\tau)\hat{c}^{\dagger}_{s\sigma}(\tau')\rangle\rangle + G^{\sigma_1}_{r_1r_1}(\tau_1,\tau_1^{\dagger})G^{\sigma}_{rs}(\tau,\tau'). \tag{2.7}$$

This will enable us to generate higher-order Green's functions in terms of lower-order ones and their functional derivatives.

The equation of motion of the adsorbate Green's function is easily shown to be

$$\left(i\frac{\partial}{\partial\tau} - \epsilon_a - X^{\sigma}_{a}(\tau)\right)G^{\sigma}_{aa}(\tau,\tau') = \delta(\tau-\tau') + U\langle\langle \hat{n}_{a,-\sigma}(\tau)\hat{c}_{a\sigma}(\tau)\hat{c}^{\dagger}_{a\sigma}(\tau')\rangle\rangle + \sum_{i} V_{ai}G^{\sigma}_{ia}(\tau,\tau') + \sum_{i} K_{ai}\langle\langle \hat{n}_i(\tau)\hat{c}_{a\sigma}(\tau)\hat{c}^{\dagger}_{a\sigma}(\tau')\rangle\rangle. \tag{2.8}$$

In terms of functional derivatives, we can rewrite (2.8) in the form

$$[G^{0\sigma}_{aa}(\tau,\bar{\tau})]^{-1}G^{\sigma}_{aa}(\bar{\tau},\tau') = \delta(\tau-\tau') + \sum_{i} V_{ai}G^{\sigma}_{ia}(\tau,\tau') + U\frac{\delta iG^{\sigma}_{aa}(\tau,\tau')}{\delta X^{-\sigma}_{a}(\tau)} + \Sigma^{(1)\sigma}_{a}(\tau,\bar{\tau})G^{\sigma}_{aa}(\bar{\tau},\tau') + \sum_{i} K_{ai}\left(\frac{\delta}{\delta X^{\sigma}_{i}(\tau)} + \frac{\delta}{\delta X^{-\sigma}_{i}(\tau)}\right)iG^{\sigma}_{aa}(\tau,\tau'), \tag{2.9}$$

where we have defined the first-order (Hartree) self-energy

$$\Sigma^{(1)\sigma}_{a}(\tau,\tau') \equiv -UiG^{-\sigma}_{aa}(\tau,\tau^{\dagger})\delta(\tau-\tau') - \sum_{i} K_{ai}i[G^{\sigma}_{ii}(\tau,\tau^{\dagger}) + G^{-\sigma}_{ii}(\tau,\tau^{\dagger})]\delta(\tau-\tau') \tag{2.10}$$

and the inverse of the noninteracting adatom Green's function is given by

$$[G_{aa}^{0\sigma}(\tau,\tau')]^{-1}\equiv\left(i\frac{\partial}{\partial\tau}-\epsilon_a-X_a^\sigma(\tau)\right)\delta(\tau-\tau')\,. \tag{2.11}$$

A bar over time coordinates means that these are integrated from 0 to $-i\beta$.

The hopping term in (2.9) involves the mixed metal-adatom Green's function G_{ia}^σ and this cannot be expressed as a functional derivative of the adatom Green's function. The equation of motion for G_{ir}^σ is given by

$$\begin{aligned}\left(i\frac{\partial}{\partial\tau}-X_i^\sigma(\tau)\right)G_{ir}^\sigma(\tau,\tau')&=\delta(\tau-\tau')\delta_{ir}+\sum_l T_{il}G_{lr}^\sigma(\tau,\tau')+\sum_l v_{il}\langle\langle\hat{n}_l(\tau)\hat{c}_{i\sigma}(\tau)\hat{c}_{r\sigma}(\tau')\rangle\rangle\\&\quad+V_{ai}G_{ar}^\sigma(\tau,\tau')+K_{ai}\langle\langle\hat{n}_a(\bar{\tau})\hat{c}_{i\sigma}(\tau)\hat{c}_{r\sigma}^\dagger(\tau')\rangle\rangle\,.\end{aligned} \tag{2.12}$$

This is valid for $r=a$ (adatom) or $r=j$ (metal electron). This equation can be rewritten in the form

$$\begin{aligned}\sum_j[\tilde{G}_{ij}^\sigma(\tau,\bar{\tau})]^{-1}G_{jr}^\sigma(\bar{\tau},\tau')&=\delta(\tau-\tau')\,\delta_{ir}+V_{ai}G_{ar}^\sigma(\tau,\tau')-\sum_l v_{il}\left(\frac{\delta}{\delta X_l^\sigma(\tau)}+\frac{\delta}{\delta X_l^{-\sigma}(\tau)}\right)iG_{ir}^\sigma(\tau,\tau')\\&\quad-K_{ai}\left(\frac{\delta}{\delta X_a^\sigma(\tau)}+\frac{\delta}{\delta X_a^{-\sigma}(\tau)}\right)iG_{ir}^\sigma(\tau,\tau')\,,\end{aligned} \tag{2.13}$$

where we have introduced

$$\begin{aligned}[\tilde{G}_{ij}^\sigma(\tau,\tau')]^{-1}\equiv\Bigg[\Bigg(i\frac{\partial}{\partial\tau}-X_i^\sigma(\tau)+i\sum_l v_{il}[G_{ll}^\sigma(\tau,\tau^\dagger)+G_{ll}^{-\sigma}(\tau,\tau^\dagger)]\\+K_{ai}\{i[G_{aa}^\sigma(\tau,\tau^\dagger)+G_{aa}^{-\sigma}(\tau,\tau^\dagger)]-1\}\Bigg)\delta_{ij}-T_{ij}\Bigg]\delta(\tau-\tau')\,.\end{aligned} \tag{2.14}$$

The function $\tilde{G}_{ij}^\sigma$ is the inverse of the metal Green's function G_{ij}^σ in the Hartree approximation in so far as v and K are concerned. However, we emphasize that (2.13) is *exact*.

It is clear that (2.9) and (2.13) with $r=a$ give a closed system of coupled equations for G_{aa}^σ, G_{ia}^σ, and their functional derivatives. These equations can be solved to any degree of accuracy desired by simple iteration. At the end of the calculation, the auxiliary fields X_r^σ are set to zero ($\hat{S}=1$).

In solving (2.9) and (2.13), it is convenient to define inverse Green's functions

$$\begin{aligned}\sum_l[G_{il}^\sigma(\tau,\bar{\tau})]^{-1}G_{lj}^\sigma(\bar{\tau},\tau')&=\delta(\tau-\tau')\delta_{ij}\,,\\ [G_{aa}^\sigma(\tau,\bar{\tau})]^{-1}G_{aa}^\sigma(\bar{\tau},\tau')&=\delta(\tau-\tau')\,.\end{aligned} \tag{2.15}$$

The self-energies are given by the appropriate Dyson equations

$$\begin{aligned}[G_{ij}^\sigma(\tau,\tau')]^{-1}&=[G_{ij}^{0\sigma}(\tau,\tau')]^{-1}-\Sigma_{ij}^\sigma(\tau,\tau')\,,\\ [G_{aa}^\sigma(\tau,\tau')]^{-1}&=[G_{aa}^{0\sigma}(\tau,\tau')]^{-1}-\Sigma_a^\sigma(\tau,\tau')\,.\end{aligned} \tag{2.16}$$

By the usual manipulations,[9] (2.9) can be rewritten

$$\begin{aligned}G_{aa}^\sigma(\tau,\tau')&=G_{aa}^{0\sigma}(\tau,\tau')+\sum_i G_{aa}^{0\sigma}(\tau,\bar{\tau}_1)V_{ai}G_{ia}^\sigma(\bar{\tau}_1,\tau')\\&\quad+G_{aa}^{0\sigma}(\tau,\bar{\tau}_1)\Sigma_a^{(1)\sigma}(\bar{\tau}_1,\bar{\tau}_2)G_{aa}^\sigma(\bar{\tau}_2,\tau')-G_{aa}^{0\sigma}(\tau,\bar{\tau}_1)\Bigg[UiG_{aa}^\sigma(\bar{\tau}_1,\bar{\tau}_3)\frac{\delta\Sigma_a^\sigma(\bar{\tau}_3,\bar{\tau}_4)}{\delta X_a^{-\sigma}(\bar{\tau}_1)}\\&\quad+\sum_i K_{ai}iG_{aa}^\sigma(\bar{\tau}_1,\bar{\tau}_3)\left(\frac{\delta}{\delta X_i^\sigma(\bar{\tau}_1)}+\frac{\delta}{\delta X_i^{-\sigma}(\bar{\tau}_1)}\right)\Sigma_a^\sigma(\bar{\tau}_3,\bar{\tau}_4)\Bigg]G_{aa}^\sigma(\bar{\tau}_4,\tau')\,.\end{aligned} \tag{2.17}$$

If it were not for the second term on the right-hand side involving the mixed adatom-metal Green's function G_{ia}, we could read from (2.17) a self-consistent integral equation for the adatom self-energy $\Sigma_a^\sigma(\tau,\tau')$. The equation of motion for $G_{ii'}^\sigma$ in (2.13) may be rewritten in the form

$$\begin{aligned}G_{ii'}^\sigma(\tau,\tau')&=\tilde{G}_{ii'}^\sigma(\tau,\tau')(1-\delta_{i'a})+\sum_j\tilde{G}_{ij}^\sigma(\tau,\bar{\tau}_1)V_{ja}G_{ai'}^\sigma(\bar{\tau}_1,\tau')\\&\quad-i\sum_{j,l}\tilde{G}_{ij}^\sigma(\tau,\bar{\tau}_1)v_{jl}\left(\frac{\delta}{\delta X_l^\sigma(\bar{\tau}_1)}+\frac{\delta}{\delta X_l^{-\sigma}(\bar{\tau}_1)}\right)G_{ji'}^\sigma(\bar{\tau}_1,\tau')\\&\quad-i\sum_j\tilde{G}_{ij}^\sigma(\tau,\bar{\tau}_1)K_{aj}\left(\frac{\delta}{\delta X_a^\sigma(\bar{\tau}_1)}+\frac{\delta}{\delta X_a^{-\sigma}(\bar{\tau}_1)}\right)G_{ji'}^\sigma(\bar{\tau}_1,\tau')\,.\end{aligned} \tag{2.18}$$

In the absence of the Coulomb interactions v and K, the mixed Green's function G_{ia} is given exactly by the second term in (2.18). This is not the case in our problem, but we could use this as a first approximation to G_{ia} and proceed to calculate the functional derivatives in (2.18) by iteration. We shall use the lowest-order approximation

$$G^\sigma_{ia}(\tau,\tau')=\sum_j \tilde{G}^\sigma_{ij}(\tau,\bar{\tau}_1)V_{ja}G^\sigma_{aa}(\bar{\tau}_1,\tau')\,. \qquad (2.19)$$

We might note that this is exact *if* we assume that the hopping term V only couples to the d electrons while the Coulomb interactions v and K only involve the s electrons.

Using (2.19) in (2.17), we can read off a self-consistent equation for the adatom self-energy from (2.16):

$$\begin{aligned}\Sigma^\sigma_a(\tau,\tau')=&\sum_{i,j} V_{ai}\tilde{G}^\sigma_{ij}(\tau,\tau')V_{ja}\\&+\Sigma^{(1)\sigma}_a(\tau,\tau')\\&+UiG^\sigma_{aa}(\tau,\bar{\tau}_1)\frac{\delta\Sigma^\sigma_a(\bar{\tau}_1,\tau')}{\delta X^{-\sigma}_a(\tau_1)}\\&+\sum_i K_{ai}iG^\sigma_{aa}(\tau,\bar{\tau}_1)\left(\frac{\delta}{\delta X^\sigma_i(\tau_1)}\right.\\&\left.+\frac{\delta}{\delta X^{-\sigma}_i(\tau)}\right)\Sigma^\sigma_a(\bar{\tau}_1,\tau')\,.\end{aligned} \qquad (2.20)$$

To obtain Σ^σ_a to second order in U and K, we need only compute the functional derivatives using Σ^σ_a correct to first order in U and K. The final result is

$$\begin{aligned}\Sigma^{(2)\sigma}_a(\tau-\tau')=&\sum_{i,j}K_{ai}K_{aj}iG^\sigma_{aa}(\tau-\tau')\chi^n_{ij}(\tau-\tau')\\&+U^2iG^\sigma_{aa}(\tau-\tau')\chi^\sigma_{aa}(\tau-\tau')\\&+\sum_i UK_{ai}iG^\sigma_{aa}(\tau-\tau')\chi^{-\sigma}_{ai}(\tau-\tau')\\&+\sum_i K_{ai}UiG^\sigma_{aa}(\tau-\tau')\chi^{-\sigma}_{ia}(\tau-\tau')\,.\end{aligned} \qquad (2.21)$$

Here the response function of the adatom electrons is given by

$$\begin{aligned}\chi^\sigma_{aa}(\tau_1,\tau_2)&\equiv-i\delta G^\sigma_{aa}(\tau_2,\tau_2^\dagger)/\delta X^\sigma_a(\tau_1)\\&=-i\langle T\{[\hat{n}_{a\sigma}(\tau_1)-\langle\hat{n}_{a\sigma}\rangle][\hat{n}_{a\sigma}(\tau_2)-\langle\hat{n}_{a\sigma}\rangle]\}\rangle\,,\end{aligned} \qquad (2.22)$$

while the density response function of the metal electrons is

$$\begin{aligned}\chi^n_{ij}(\tau_1,\tau_2)&\equiv-i\left(\frac{\delta\tilde{G}^\sigma_{jj}(\tau_2,\tau_2^\dagger)}{\delta X^\sigma_i(\tau_1)}+\frac{\delta\tilde{G}^{-\sigma}_{jj}(\tau_2,\tau_2^\dagger)}{\delta X^{-\sigma}_i(\tau_1)}\right)\\&=-i\langle T\{[\hat{n}_i(\tau_1)-\langle\hat{n}_i\rangle][\hat{n}_j(\tau_2)-\langle\hat{n}_j\rangle]\}\rangle\,.\end{aligned} \qquad (2.23)$$

In the last step in (2.23) we have used the fact that $(\delta G^\sigma_{jj}/\delta X^{-\sigma}_i)$ vanishes. The mixed density response functions are defined by

$$\begin{aligned}\chi^\sigma_{ai}(\tau_1,\tau_2)&\equiv-i\delta\tilde{G}^\sigma_{ii}(\tau_2,\tau_2^\dagger)/\delta X^\sigma_a(\tau_1)\\&=-i\langle T[\hat{n}_{a\sigma}(\tau_1)-\langle\hat{n}_{a\sigma}\rangle][\hat{n}_{i\sigma}(\tau_2)-\langle\hat{n}_{i\sigma}\rangle]\rangle\,.\end{aligned} \qquad (2.24)$$

It is easy to verify that these mixed density response functions χ_{ai} are at least of order K and thus the last two terms in (2.21) are really of order UK^2. We have let the auxiliary fields X^σ_r go to zero and as a result, all functions in (2.21) only depend on the time difference. We recall that, to second order in V, the hopping self-energy is given by

$$\Sigma^{\mathrm{hop}}_a(\tau-\tau')=\sum_{i,j}V_{ai}V_{ja}\tilde{G}_{ij}(\tau-\tau')\,. \qquad (2.25)$$

The second term in (2.21) gives the expected adatom self-energy to second order in U^2. This arises from the adatom electron (of spin σ) exciting a density fluctuation in electrons of spin σ on the adatom. This adatom self-energy has been considered at length in a recent paper by Hertz and Handler.[26] It is this term which Schönhammer[13,27] has used in going past the simple Hartree-Fock (HF) approximation for U. Schönhammer has pointed out that it makes a significant improvement on the HF solution. In particular, in the symmetric case ($\epsilon_a=\epsilon_F-\frac{1}{2}U$), it gives the correct atomic limit for $U\gg V$. Thus it is an alternative to the Brenig-Schönhammer approximation to be discussed in Sec. III.

The first-order self-energy (2.10) is given explicitly by

$$\begin{aligned}\Sigma^{(1)\sigma}_a(\tau-\tau')=&\,U\langle\hat{n}_{a-\sigma}\rangle\delta(\tau-\tau')\\&+\sum_i K_{ai}\langle\hat{n}_i\rangle\delta(\tau-\tau')\,.\end{aligned} \qquad (2.26)$$

It is important, however, to realize that the thermal average $\langle\hat{n}_{a\sigma}\rangle$ includes the perturbation produced by the metal, while $\langle\hat{n}_i\rangle$ includes the effect of the adatom on the metal substrate. Rather than computing $\langle\hat{n}_i\rangle$ directly from the equations of motion for $G^\sigma_{ii}(\tau,\tau^\dagger)$, it is simpler to use linear response theory to obtain the perturbation to lowest order in K. One finds

$$\langle\hat{n}_i\rangle=\langle\hat{n}_i\rangle_0+\sum_j\chi^n_{ij}(\omega=0)K_{ja}(\langle\hat{n}_a\rangle-1)\,. \qquad (2.27)$$

It is well known that if we had kept the ion-ion and ion-electron interaction terms in describing the metal, they would give rise to self-energy contributions which exactly cancel the Hartree self-energy arising from the $\langle n_i\rangle_0$ term in (2.27). In this connection, we also note that the Coulomb coupling of the metal ions to adatom electron is canceled out by their coupling to the adatom nuclear charge.

We Fourier transform with respect to the imaginary time variable in the standard way[25]

$$A(i\omega_n)=\int_0^{-i\beta} d\tau\exp(-\omega_n\tau)A(\tau)\,, \qquad A(\tau)=\frac{1}{-i\beta}\sum_n \exp(\omega_n\tau)A(i\omega_n)\,, \tag{2.28}$$

where $\omega_n=n\pi/\beta$ with $n=0$, ±2, ±4 for response functions and $n=\pm1$, ±3, ±5 for Green's functions. The Fourier coefficients can be analytically continued to real frequencies ($i\omega_n\to\omega+i0^+$). The final results are

$$\Sigma_a^{(1)\sigma}(\omega)=U\langle\hat{n}_{a-\sigma}\rangle+\sum_{ij}K_{ai}K_{aj}\chi^n_{ij}(\omega=0)(\langle\hat{n}_a\rangle-1)\,, \tag{2.29}$$

and (keeping only the term involving K)

$$\Sigma_a^{(2)\sigma}(\omega)=-\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\sum_{i,j}K_{ai}K_{aj}\times\left(\mathrm{Im}G^\sigma_{aa}(\omega')\chi^n_{ij}(\omega-\omega')\tanh\frac{\beta\omega'}{2}+\mathrm{Im}\chi^n_{ij}(\omega')G^\sigma_{aa}(\omega-\omega')\,\mathrm{cotanh}\frac{\beta\omega'}{2}\right). \tag{2.30}$$

For completeness, we have given the finite-temperature expression ($\beta=1/k_BT$).[28] These adatom self-energies have a simple diagrammatic representation, as shown in Fig. 1. $\Sigma^{(1)}$ corresponds to a direct (or Hartree) term while $\Sigma^{(2)}$ is an exchange self-energy, the effective interaction being given by

$$K(\omega)=\sum_{i,j}K_{ai}\chi^n_{ij}(\omega)K_{ja}\,. \tag{2.31}$$

The direct term vanishes if $\langle\hat{n}_a\rangle=1$ and describes the shift of the adsorbate electron levels due to the interaction of the average charge on the adatom with its image change. The exchange term involves a dynamically screened interaction mediated by the charge fluctuations of the substrate conduction electrons. The main advantage of the functional differentiation method over decoupling methods[29] is that it leads to self-energy approximations which are capable of a diagrammatic interpretation and which involve the full adatom Green's function. This allows us to calculate the adatom self-energies to order K^2 self-consistently, if this is important.

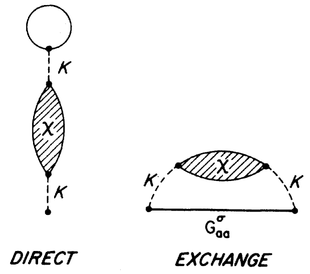

FIG. 1. Diagrammatic representation of adatom self-energy to second order in the adatom-metal Coulomb interaction K. χ is the density response function of the substrate [see (2.29) and (2.30)].

We might remark that Pfuff and Appel[30] have recently discussed the adatom self-energy treating all Coulomb interactions (v, U, and K) in a self-consistent Hartree-Fock approximation. Their work is an extension of earlier work by Grimley,[31] and Einstein.[32] In addition, Bagchi and Cohen[33] as well as Bell and Madhukar[29] have considered the Coulomb interaction v between the substrate conduction electrons but only to first order. Our analysis goes beyond such studies to include adatom self-energy terms which are second order in K and U and, in principle, to all orders in v through the full density response function χ of the metal substrate. In order to include the dynamical effect of substrate charge fluctuations such as surface plasmons, it is necessary to go beyond the Hartree-Fock approximations used by previous authors.

As a first approximation, one can calculate $\Sigma_\sigma^{(2)}(\omega)$ in (2.30) using the Hartree-Fock $G^\sigma_{aa}(\omega)$. This is given by the well-known expression[2,3]

$$G^\sigma_{aa}(\omega)=[\omega-\epsilon_a-U\langle\hat{n}_{a-\sigma}\rangle-\Gamma(\omega)]^{-1}\,. \tag{2.32}$$

The density $\langle\hat{n}_{a-\sigma}\rangle$ must be determined self-consistently from $G^\sigma_{aa}(\omega)$ using

$$\langle\hat{n}_{a\sigma}\rangle=-\frac{1}{\pi}\int_{-\infty}^{\epsilon_F} d\omega\,\mathrm{Im}G^\sigma_{aa}(\omega+i0^+)\,. \tag{2.33}$$

The hopping self-energy is given by

$$\Gamma(\omega)\equiv\Sigma_a^{\mathrm{hop}}(\omega)=\sum_{i,j}V_{ai}V_{ja}\tilde{G}_{ij}(\omega)\,, \tag{2.34}$$

where $\tilde{G}_{ij}(\omega)$ is the metal Green's function describing the metal substrate electrons. Since our major interest is in the effect of the conduction-electron charge fluctuations, we shall content ourselves with the often-used one-dimensional tight-binding chain with the chemisorbed atom at the end. The resulting expression for $\Gamma(\omega)$ is summarized in an Appendix.

For later use, we conclude this section with a few remarks about the HF Green's function and its relation to the correct atomic limit. In the absence of the hopping interaction $[\Gamma(\omega)=0]$, the HF adatom Green's function given by (2.32) has a single pole at the Hartree-Fock energy

$$\epsilon_{a\sigma}^{\mathrm{HF}}=\epsilon_a+U\langle\hat{n}_{a-\sigma}\rangle\,. \tag{2.35}$$

In this case, of course, the adatom is completely uncoupled from the metal substrate, and we expect (say)

$$\langle\hat{n}_{a\uparrow}\rangle=1\,,\quad\langle\hat{n}_{a\downarrow}\rangle=0\,. \tag{2.36}$$

Hence, defining the adatom spectral density by

$$N_\sigma(\omega)=-2\,\mathrm{Im}G_{aa}^{\sigma}(\omega+i0^+)\,, \tag{2.37}$$

we would have

$$\begin{aligned}N_\uparrow(\omega)&=2\pi\delta(\omega-\epsilon_a)\,,\\ N_\downarrow(\omega)&=2\pi\delta[\omega-(\epsilon_a+U)]\,.\end{aligned} \tag{2.38}$$

The energy level ϵ_a is referred to as the atomic ionization level ϵ_a+U is the atomic affinity level.

In the presence of the hopping self-energy, the adatom Green's function will have poles at $\omega=\Omega$ where the equation

$$\Omega-\epsilon_a-U\langle\hat{n}_{a-\sigma}\rangle=\mathrm{Re}\Gamma(\Omega) \tag{2.39}$$

has solutions outside the d band, i.e., where $\mathrm{Im}\Gamma(\omega)=0$. We may have zero, one, or two split-off peaks depending on the strength of V and the magnitude of the Hartree-Fock energy ϵ_a^{HF}. In addition, we always have a solution of (2.39) which lies inside the d band, but this only gives rise to a broad resonance. When the bandwidth $W\gg V$ and $\langle\hat{n}_{a\uparrow}\rangle=\langle\hat{n}_{a\downarrow}\rangle$, there is only a single broad peak in $N(\omega)$ near the Hartree-Fock energy $\epsilon_a^{\mathrm{HF}}=\epsilon_a+\frac{1}{2}U$.

The value of $\langle\hat{n}_{a-\sigma}\rangle$ must be determined self-consistently using (2.33). A convenient way of doing this is to plot $\langle\hat{n}_{a\uparrow}\rangle$ as a function of $\langle\hat{n}_{a\downarrow}\rangle$ and $\langle\hat{n}_{a\downarrow}\rangle$ as a function of $\langle\hat{n}_{a\uparrow}\rangle$, the intersections giving self-consistent solutions. We emphasize that the HF result is really only appropriate for $V\gtrsim U$. When $V\ll U$, one often finds *magnetic* solutions $\langle n_{a\uparrow}\rangle\neq\langle\hat{n}_{a\downarrow}\rangle$ as well as *nonmagnetic* solutions $\langle n_{a\uparrow}\rangle=\langle n_{a\downarrow}\rangle$ and the magnetic solutions correspond to a lower total energy. The Hartree-Fock approximation, of course, can no longer be trusted in this regime where magnetic solutions are obtained. In actual fact, in the limit $V\to0$, the exact Green's function can be found exactly. Instead of (2.32), we have

$$G_{aa}^{0\sigma}(\omega)=\frac{1-\langle\hat{n}_{a-\sigma}\rangle}{\omega-\epsilon_a}+\frac{\langle\hat{n}_{a-\sigma}\rangle}{\omega-(\epsilon_a+U)}\,. \tag{2.40}$$

This can be used to find $\langle\hat{n}_{a\sigma}\rangle$ from (2.33). At $T=0$ K, for $\epsilon_a<\epsilon_F$ and $\epsilon_a+U>\epsilon_F$, one finds the magnetic solutions (2.36) as well as nonmagnetic solutions given by

$$\langle n_{a\uparrow}\rangle=\langle n_{a\downarrow}\rangle=\tfrac{1}{2}\,. \tag{2.41}$$

In this case, however, both (2.36) and (2.41) are degenerate and one must choose the correct nonmagnetic solution before turning on the hopping interaction (just as in degenerate perturbation theory). Thus in the atomic limit $V\to0$, the adatom spectral density is given by

$$N^0(\omega)=\pi\{\delta(\omega-\epsilon_a)+\delta[\omega-(\epsilon_a+U)]\} \tag{2.42}$$

and not by the Hartree-Fock result (2.38). Equation (2.40) is the starting point of the Brenig-Schönhammer approximation[10,29] to be discussed in Sec. III. This is more appropriate in the atomic limit where $U\gg V$ and, as we shall see, only exhibits nonmagnetic solutions.

III. BRENIG-SCHÖNHAMMER APPROXIMATION

Here we turn to a discussion of the effect of substrate charge fluctuations on the adatom spectral density which is appropriate to the case $V\ll U$, such as occurs in chemisorption on transition metals. This regime is more complicated because one must develop a theory which has the correct atomic limit (2.40) when the adatom is uncoupled from the metal $(V,K\to0)$. The procedure we adopt for treating V will be that used by Brenig and Schönhammer.[3,10] Defining the Hubbard operators

$$\hat{\psi}_{\alpha\sigma}\equiv\begin{cases}\hat{n}_{a-\sigma}\hat{c}_{a\sigma}\,, & \alpha=+\,,\\ (1-\hat{n}_{a-\sigma})\hat{c}_{a\sigma}\,, & \alpha=-1\,,\end{cases} \tag{3.1}$$

we shall base our analysis on the so-called Hubbard Green's functions $(\alpha,\beta=\pm)$

$$\mathcal{G}_{\alpha\beta}^{\sigma}(\tau-\tau')=-i\,\frac{\langle T[\hat{S}\hat{\psi}_{\alpha\sigma}(\tau)\hat{\psi}_{\beta\sigma}^{\dagger}(\tau')]\rangle}{\langle T(\hat{S})\rangle} \tag{3.2}$$

$$\equiv\langle\langle\hat{\psi}_{\alpha\sigma}(\tau)\hat{\psi}_{\beta\sigma}^{\dagger}(\tau')\rangle\rangle\,, \tag{3.3}$$

where $\hat{S}$ is defined as in (2.6). We shall develop equations of motion for this 2×2 matrix Green's function using a simple decoupling method for the hopping self-energy and functional differentiation for the Coulomb self-energy terms. We note that

$$\hat{c}_{a\sigma}=\sum_{\alpha}\hat{\psi}_{\alpha\sigma}\,,\quad\hat{c}_{a\sigma}^{\dagger}=\sum_{\alpha}\hat{\psi}_{\alpha\sigma}^{\dagger}\,, \tag{3.4}$$

and thus the real adatom Green's function is given by

$$G_{aa}^{\sigma}(\tau-\tau')=\sum_{\alpha,\beta}\mathcal{G}_{\alpha\beta}^{\sigma}(\tau-\tau')\,. \tag{3.5}$$

The advantage of working with the more complicated matrix Green's functions $\mathcal{G}_{\alpha\beta}^{\sigma}$ becomes clear when we write the equation of motion

$$\left(i\frac{\partial}{\partial\tau}\epsilon_\alpha - X^\sigma_a(\tau)\right)\mathcal{G}^\sigma_{\alpha\beta}(\tau-\tau') = i\langle\langle n_{\alpha\sigma}(\tau)\rangle\rangle\delta_{\alpha\beta}\delta(\tau-\tau') + \sum_j V_{aj}\langle\langle\hat{n}_{\alpha\sigma}(\tau)\hat{c}_{j\sigma}(\tau)\hat{\psi}^\dagger_{\beta\sigma}(\tau')\rangle\rangle$$
$$-\alpha\sum_j V_{ja}\langle\langle\hat{c}_{j-\sigma}(\tau)\hat{c}_{a-\sigma}(\tau)\hat{c}_{a\sigma}(\tau)\hat{\psi}^\dagger_{\beta\sigma}(\tau')\rangle\rangle + \alpha\sum_j V_{aj}\langle\langle\hat{c}^\dagger_{a-\sigma}(\tau)\hat{c}_{j-\sigma}(\tau)\hat{c}_{a\sigma}(\tau)\hat{\psi}^\dagger_{\beta\sigma}(\tau')\rangle\rangle$$
$$+\sum_i K_{ai}\langle\langle\hat{n}_i(\tau)\hat{\psi}_{\alpha\sigma}(\tau)\hat{\psi}^\dagger_{\beta\sigma}(\tau')\rangle\rangle\,, \tag{3.6}$$

where

$$\epsilon_\alpha \equiv \begin{cases}\epsilon_a + U\,, & \alpha=+\,,\\ \epsilon_a\,, & \alpha=-\end{cases} \tag{3.7}$$

and

$$\hat{n}_{\alpha\sigma} \equiv \begin{cases}\hat{n}_{a-\sigma}\,, & \alpha=+\,,\\ 1-\hat{n}_{a-\sigma}\,, & \alpha=-\,.\end{cases} \tag{3.8}$$

If we consider the isolated adatom ($V, K\to 0$) and set the auxiliary fields X^σ_a to zero, (3.6) is easily solved and we find

$$\mathcal{G}^0_{\alpha\beta}(\omega) = [\langle n_{\alpha\sigma}\rangle_0/(\omega-\epsilon_\alpha)]\delta_{\alpha\beta}\,. \tag{3.9}$$

Inserting this into (3.5), we obtain the exact atomic limit adatom Green's function (2.40).

A. Hopping self-energy

We next set up equations of motion for the Green's functions entering into the hopping contributions in (3.6) and solve these by making a simple HF decoupling approximation for the metal electrons. One finally finds that the three hopping terms in (3.6) can be written[23]

$$-\alpha\sum_j V_{ja}G^0_{jA}(\tau-\tau')\langle\hat{c}^\dagger_{j-\sigma}\hat{\psi}^\dagger_{-\beta-\sigma}\rangle$$
$$+\alpha\sum_{ij} V_{ai}\tilde{G}_{ij}(\tau-\tau')\langle\hat{\psi}^\dagger_{\beta-\sigma}\hat{c}_{j-\sigma}\rangle$$
$$+\sum_\gamma\Big(\sum_{i,j} V_{ai}\tilde{G}_{ij}(\tau-\bar{\tau})V_{ja}\delta_{\alpha\gamma}$$
$$+\alpha\sum_j V_{ja}G^0_{jA}(\tau-\bar{\tau})V_{aj}(\delta_{+,\gamma}-\langle\hat{n}_{j-\sigma}\rangle)$$
$$+\alpha\sum_{ij} V_{ai}\tilde{G}_{ij}(\tau-\bar{\tau})V_{ja}(\delta_{+,\gamma}-\langle\hat{n}_{j,-\sigma}\rangle)\Big)$$
$$\times G^\sigma_{\gamma\beta}(\bar{\tau},\tau')\,, \tag{3.10}$$

where the metal electron Green's function is given by [see (2.12)]

$$i\frac{\partial}{\partial\tau}\tilde{G}_{ij}(\tau-\tau') = \delta(\tau-\tau')\delta_{ij} + \sum_l T_{il}\tilde{G}_{lj}(\tau-\tau')\,, \tag{3.11}$$

and G^0_{iA} is defined by

$$\left(i\frac{\partial}{\partial\tau} - (\epsilon_+ + \epsilon_-)\right)G^0_{iA}(\tau-\tau') = \delta(\tau-\tau') + \sum_j T_{ij}G^0_{jA}(\tau-\tau')\,. \tag{3.12}$$

These results are identical to that obtained by Dworin[34] in connection with the Anderson model of a magnetic impurity and, independently, by Bell and Madkukar.[29] However, the first two terms on the right-hand side of (3.10) [$\equiv\Delta n^\sigma_{\alpha\beta}(\tau-\tau')$] are not in a form for which we can write down a Dyson equation of motion and hence find a self-energy $\Sigma^\sigma_{\alpha\beta}(\tau-\tau')$.

Our procedure is to rewrite $\Delta n^\sigma_{\alpha\beta}$ in the form

$$\sum_{\gamma,\delta}[\Delta n^\sigma_{\alpha\gamma}(\tau-\bar{\tau}_1)\mathcal{G}^{-1}_{\gamma\delta}(\bar{\tau}_1-\bar{\tau})]\mathcal{G}_{\delta\beta}(\bar{\tau}-\tau') \tag{3.13}$$

and expand the expression in the square brackets to second order in V. The end result is that we find the hopping terms on the right-hand side of (3.6) can be written in the form

$$\sum_\delta \Sigma^{\text{hop}}_{\alpha\delta}(\tau-\bar{\tau})\mathcal{G}_{\delta\beta}(\bar{\tau}-\tau')\,, \tag{3.14}$$

where the 2×2 matrix hopping self-energy is given by (after Fourier transforming)

$$\Sigma^{\text{hop}}_{\alpha\beta}(\omega) = \begin{pmatrix} 2\Gamma(\omega)+\Delta(\omega) & -[\Gamma(\omega)+\Delta(\omega)] \\ -[\Gamma(\omega)+\Delta(\omega)] & 2\Gamma(\omega)+\Delta(\omega)\end{pmatrix}\,. \tag{3.15}$$

Here $\Gamma(\omega)$ is the hopping self-energy which arose in the Hartree-Fock approximation [see (2.34)]

$$\Gamma(\omega) = \sum_k \frac{|V_{ak}|^2}{\omega-\epsilon_k}\,, \tag{3.16}$$

while

$$\Delta(\omega) = \sum_k |V_{ak}|^2\left(\frac{f(\epsilon_k)-f(\epsilon_+)}{\epsilon_k-\epsilon_+} - \frac{f(\epsilon_k)-f(\epsilon_-)}{\epsilon_k-\epsilon_-}\right)\,. \tag{3.17}$$

Here $f(\epsilon)$ is the Fermi distribution, and ϵ_k is the metal electron dispersion relation. In our work, we shall evaluate $\Gamma(\omega)$ and $\Delta(\omega)$ using the one-dimensional tight-binding model summarized in the Appendix. Our expressions for the matrix elements of $\Sigma^{\text{hop}}_{\alpha\beta}(\omega)$ are identical to those of Brenig and Schönhammer (BS)[10] if we set $\langle \hat{n}_{a\sigma} \rangle = \frac{1}{2}$ in their results. In neutral chemisorption such as we are interested in, this should not make too much difference because the charge transfer is small.

Before turning to the determination of the self-energy due to the Coulomb coupling term K in (3.6), it will be useful to briefly remark on some of the qualitative features of $G^{\sigma}_{aa}(\omega)$ which results from the BS theory. Introducing the auxiliary Hubbard Green's function

$$\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\omega) \equiv \mathcal{G}^{\sigma}_{\alpha\beta}(\omega) \langle n_{\beta\sigma} \rangle^{-1} , \tag{3.18}$$

one finds that it satisfies the 2×2 Dyson equation

$$(\hbar\omega - \epsilon_{\alpha}) \hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \sum_{\gamma} \Sigma^{\text{hop}}_{\alpha\gamma}(\omega) \hat{\mathcal{G}}_{\gamma\beta}(\omega) . \tag{3.19}$$

Solving this using (3.15), we find from (3.5) that the adatom Green's function is given by

$$G^{\sigma}_{a\sigma}(\omega) = \frac{\omega - \epsilon_a - U(1 - \langle n_{a-\sigma} \rangle) - R - S}{(\omega - \epsilon_a - R)(\omega - \epsilon_a - U - R) - S^2} , \tag{3.20}$$

where $R \equiv 2\Gamma(\omega) + \Delta(\omega)$ and $S \equiv \Gamma(\omega) + \Delta(\omega)$. We recall that (3.20) treats U exactly but V perturbatively. The poles of $G^{\sigma}_{aa}(\omega)$ are given by the solutions of

$$(\omega - \epsilon_a - R)(\omega - \epsilon_a - U - R) - S^2 = 0 \tag{3.21}$$

outside the d band [i.e., where $\text{Im}\Sigma^{\text{hop}}_{\alpha\beta}(\omega) = 0$]. It is convenient to find these isolated roots by plotting the solutions $S_{\pm}$ of (3.21) viewed as a quadratic in S,

$$S_{\pm}(\omega) = \tfrac{1}{3}\{(2\tilde{\omega} - \epsilon_+ - \epsilon_-) \pm [(2\tilde{\omega} - \epsilon_+ - \epsilon_-)^2 - 3(\tilde{\omega} - \epsilon_+)(\tilde{\omega} - \epsilon_+)]^{1/2}\} , \tag{3.22}$$

where $\tilde{\omega} \equiv \omega + \Delta$, and seeing where these solutions intersect the curve $S(\omega) = \Gamma(\omega) + \Delta(\omega)$.

As a specific case, let us consider H chemisorbed on Ni and assume (for simplicity) that the hopping interaction is mainly to the d-band electrons. Following Newns,[2] we take the d bandwidth $2W = 3.8$ eV. With the Fermi energy (−4.5 eV below the vacuum level) as our zero of energy, the top of the band is at 0.14 eV, the bottom at −3.66 eV and the band center is $\epsilon_c = -1.76$ eV. Taking $U = 12.9$ eV, we have $\epsilon_- \equiv \epsilon_a = -9.1$ eV and $\epsilon_+ \equiv \epsilon_a + U = 3.8$ eV. The strength of the hopping between the adatom and substrate (V) will be viewed as a parameter to be varied, but it is expected to be of the order of a few eV. In evaluating the hopping self-energies, we introduce a finite electron lifetime τ in our semielliptical model (see Appendix) for the d band. The origin of this broadening need not concern us, although it may be interpreted as partially due to coupling with the substrate sp-band electrons.[13] Following Brenig and Schönhammer,[10] we take $1/\tau = 1$ eV.

In Fig. 2, we plot the functions $S_{\pm}(\omega)$ given by (3.22) and S for the case $V = 3$ eV. We also show the resulting adatom density of states. In this case of small hopping, we only get two peaks (P_I and P_A), which become the atomic ionization and affinity levels for $V \to 0$. For V sufficiently large (see Fig. 3), two new solutions appear *outside* the d band (S_I and S_A). As V increases, the peaks P_I and P_A are repelled from the d band and their weight decreases, while the weight of the S_I and S_A peaks increases. Ultimately one reaches a region in which the S peaks dominate. The original atomic levels (P_I and P_A) are of zero weight and (3.20) reduces to the Hartree-Fock solution discussed in Sec. II. For intermediate "realistic" values of the hopping strength V, P_I lies below the atomic ionization level ϵ_a while S_A lies above. At the present time, it is not clear whether the experimentally observed peak in the photoemission spectra of H chemisorbed on Ni should be interpreted[29] as P_I (shifted upward by screening effects due to K—see Sec. V) or as S_A, as argued by Brenig and Schönhammer.[10]

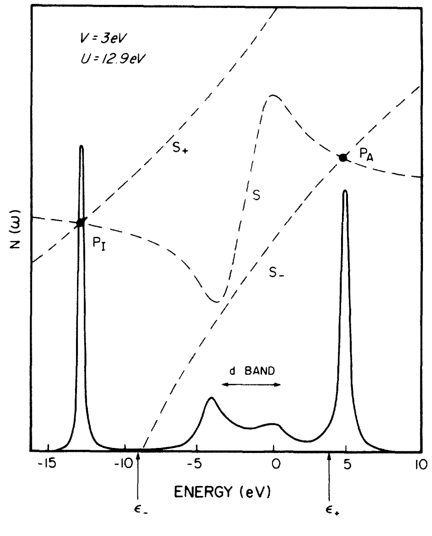

FIG. 2. Adatom spectral density $N(\omega)$ as a function of the energy ω, using the Brenig-Schöhammer approximation for the hopping self-energy. As discussed in the text, the intersections of the dashed curves give the poles of adatom Green's function in Eq. (3.20).

In concluding this brief study of the Brenig-Schönhammer approximation,[10,29] we would also like to stress that one of the satisfying features of (3.20) compared to the HF result of Newns given by (2.32) is that when one uses (2.33) to compute $\langle\hat{n}_{a,\sigma}\rangle$, the BS result never gives rise to magnetic solutions ($\langle\hat{n}_{a\uparrow}\rangle\neq\langle\hat{n}_{a\downarrow}\rangle$). This is not unexpected when one notes that in the BS approximation, the poles of $G^{\sigma}_{aa}(\omega)$ do not depend on the value $\langle\hat{n}_{a,-\sigma}\rangle$, in contrast to the poles of the Hartree-Fock result in (2.32).

In contrast to the nonsymmetrical cases shown in Figs. 2 and 3, BS only gave results for the symmetrical case where $\epsilon_a+\frac{1}{2}U=\epsilon_F$, which in our notation means $\epsilon_-=-\frac{1}{2}U$ and $\epsilon_+=\frac{1}{2}U$, with the center of the band at $\epsilon_c=0$. Moreover they took $2W=U$. The results in Figs. 2 and 3 correspond to weak chemisorption in so far as $V\ll U$.

B. Self-energy due to substrate charge fluctuations

Having now determines the hopping self-energy, we now return to the general equation of motion (3.6). Writing the last term on the right-hand side in terms of functional derivatives, the auxiliary Green's function defined in (3.18) satisfies

$$\sum_{\gamma}[\hat{\mathcal{G}}^{0\sigma}_{\alpha\gamma}(\tau,\bar{\tau})]^{-1}\hat{\mathcal{G}}^{\sigma}_{\gamma\beta}(\bar{\tau},\tau')=\delta_{\alpha\beta}\delta(\tau-\tau')+\sum_{\gamma}\Sigma^{\mathrm{hop}}_{\alpha\gamma}(\tau,\bar{\tau})\hat{\mathcal{G}}^{\sigma}_{\gamma\beta}(\bar{\tau},\tau')+\Sigma^{(1)}_{\alpha\alpha}(\tau,\bar{\tau})\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\bar{\tau},\tau')$$

$$+\sum_{j}K_{aj}\left(\frac{\delta}{\delta X^{\sigma}_{j}(\tau)}+\frac{\delta}{\delta X^{-\sigma}_{j}(\tau)}\right)i\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\tau,\tau')\,. \tag{3.23}$$

We have introduced the inverse Hubbard Green's function

$$[\hat{\mathcal{G}}^{0\sigma}_{\alpha\beta}(\tau,\tau')]^{-1}\equiv\left(i\frac{\partial}{\partial\tau}-\epsilon_{\alpha}-X^{\sigma}_{\alpha}(\tau)\right)\delta(\tau-\tau')\delta_{\alpha\beta}, \tag{3.24}$$

and $\Sigma^{(1)}_{\alpha\alpha}$ corresponds to the self-energy which is linear in K given by (2.10). We see that (3.23) is a closed Dyson equation for $\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}$. Defining

$$\sum_{\gamma}[\hat{\mathcal{G}}^{\sigma}_{\alpha\gamma}(\tau,\bar{\tau})]^{-1}\hat{\mathcal{G}}^{\sigma}_{\gamma\beta}(\bar{\tau},\tau')=\delta_{\alpha\beta}\delta(\tau-\tau')\,, \tag{3.25}$$

and the 2×2 self-energy by the usual equation

$$[\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\tau,\tau')]^{-1}=[\hat{\mathcal{G}}^{0\sigma}_{\alpha\beta}(\tau,\tau')]^{-1}-\hat{\Sigma}^{\sigma}_{\alpha\beta}(\tau,\bar{\tau})\,, \tag{3.26}$$

we find the self-energy obeys the following equation:

$$\hat{\Sigma}^{\sigma}_{\alpha\beta}(\tau,\tau')=\Sigma^{\mathrm{hop}}_{\alpha\beta}(\tau,\tau')+\Sigma^{(1)}_{\alpha\alpha}(\tau,\tau')\delta_{\alpha\beta}$$

$$+\sum_{j,\gamma}K_{aj}i\hat{\mathcal{G}}^{\sigma}_{\alpha\gamma}(\tau,\bar{\tau})$$

$$\times\left(\frac{\delta}{\delta X^{\sigma}_{j}(\tau)}+\frac{\delta}{\delta X^{-\sigma}_{j}(\tau)}\right)\hat{\Sigma}^{\sigma}_{\gamma\beta}(\bar{\tau},\tau')\,. \tag{3.27}$$

This should be compared to the analogous equation (2.19) obtained in the Hartree-Fock approximation. The Coulomb repulsion U does not appear explicitly, as it does in (2.20), because it has been incorporated exactly into $\hat{\mathcal{G}}^{0\sigma}_{\alpha\beta}$. The price we have to pay for this is the necessity to work with the 2×2 Hubbard Green's functions.

As with (2.20), (3.27) can be used to generate various approximations to the self-energy due to K by simple iteration. To second order in K, we obtain immediately

$$\Sigma^{(2)\sigma}_{\alpha\beta}(\tau,\tau')=\sum_{i,j}K_{ai}K_{aj}i\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\tau-\tau')\chi^{n}_{ij}(\tau-\tau')\,, \tag{3.28}$$

where the substrate density response function is defined in (2.23). As in the Hartree-Fock case, the nice feature of (3.27) is that the various contributions may be interpreted diagrammatically and also involve the renormalized propagators. The direct $\Sigma^{(1)}_{\alpha\alpha}$ and exchange $\Sigma^{(2)\sigma}_{\alpha\beta}$ self-energies are once again given by Fig. 1. In summary, we have (after Fourier transforming)

$$\hat{\Sigma}^{\sigma}_{\alpha\beta}(\omega)=\Sigma^{\mathrm{hop}}_{\alpha\beta}(\omega)+\Sigma^{(1)}_{\alpha\alpha}\delta_{\alpha\beta}+\Sigma^{(2)\sigma}_{\alpha\beta}(\omega)\,, \tag{3.29}$$

with

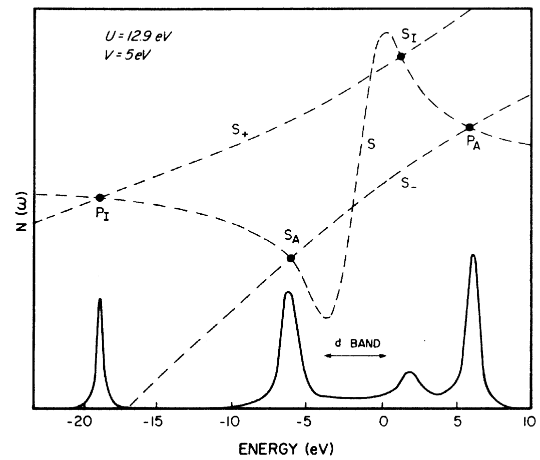

FIG. 3. Same as Fig. 2, except that now the hopping strength V is large enough to cause states (S_A and S_I) to split off from the d band.

$$\hat{\Sigma}^{(1)}_{\alpha\alpha} = K(\omega = 0)[\langle n_\alpha\rangle - 1] \ , \tag{3.30}$$

$$\Sigma^{(2)\sigma}_{\alpha\beta}(\omega) = -\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi}\,\mathrm{sgn}\,\omega' \times[\,\mathrm{Im}\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\omega')K(\omega-\omega') + \mathrm{Im}K(\omega')\hat{\mathcal{G}}^{\sigma}_{\alpha\beta}(\omega-\omega')] , \tag{3.31}$$

where the effective interaction $K(\omega)$ is defined in (2.31) and is a function of the charge fluctuation spectrum of the sp-bands of the substrate. The hopping self-energy is given by (3.15) and is determined by the appropriate metal electron Green's function. In (3.31), we have taken the $T \to 0$ limit of the analogous expression in (2.30).

IV. MODEL FOR SUBSTRATE CHARGE FLUCTUATIONS

In Sec. III, we showed that within the BS atomic limit model for chemisorption, the Coulomb interaction in (2.4) leads to "direct" and "exchange" adatom self-energies given by (3.30) and (3.31). These involve the metal substrate density response function through the effective interaction $K(\omega)$ given by (2.31). In this section, we shall calculate $K(\omega)$ and the resulting self-energies (3.30) and (3.31) using the well known classical infinite-barrier model for the metal substrate.[15-17] In this model, the surface gives rise to classical specular reflection of the electrons. The advantage of this simplified model is that the density response function χ^n_{ij} in (2.31) may be obtained analytically but it still exhibits the complete spectrum[17] of a bounded electron gas (surface plasmons, bulk plasmons, and the particle-hole spectrum). When electron-gas dispersion is completely neglected, only surface plasmons are important, as we shall see.

We assume that our substrate is a slab of thickness L and the two surfaces ($z = 0$ and $z = L$) are simulated by infinite potential barriers. While in previous chapters, it was convenient to work in a discrete (Wannier) site representation for the substrate electrons, we will now go over to a electron-gas model appropriate to the conduction electrons of interest. The site labels i now will refer to the position variables $\vec{r} = (\vec{x}_\parallel, z)$. Thus $K(\omega)$ is given by

$$K(\omega) = K_0^2 \int d\vec{r} \int d\vec{r}\,' \times \frac{e^2}{|\vec{r} - \vec{R}_a|}\,\frac{e^2}{|\vec{r}\,' - \vec{R}_a|}\,\chi^n(\vec{r}, \vec{r}\,', \omega) , \tag{4.1}$$

where the factor K_0^2 reminds us that we are working to second order in Coulomb interaction between adatom and metal sp-band electrons (of course, $K_0 = 1$). We proceed by Fourier transforming the density-density response function, with

$$\chi^n(z, z'; \vec{k}_\parallel) = \int \frac{d\vec{k}_\parallel}{(2\pi)^2} \exp[-i\vec{k}_\parallel \cdot (\vec{x}_\parallel - \vec{x}_\parallel')] \times \frac{1}{L^2} \sum_{k_z, k_z'} \cos k_z z \cos k_z' z \times \chi^n(k_z, k_z'; \vec{k}_\parallel, \omega) , \tag{4.2}$$

where

$$k_z, k_z' = n\pi/L , \quad n = 0, \pm 1, \pm 2, \ldots . \tag{4.3}$$

Using this in (4.1), calculation gives

$$K(\omega) = (K_0 e^2)^2 \int d\vec{k}_\parallel \exp(-2k_\parallel d) \times \frac{1}{L^2} \sum_{k_z, k_z'} \frac{\chi^n(k_z, k_z'; \vec{k}_\parallel, \omega)}{(k_\parallel^2 + k_z^2)(k_\parallel^2 + k_z'^2)} [1 \mp \exp(-k_\parallel L)]^2 , \tag{4.4}$$

where we have assumed that the adatom is at $Z_a = -d$. We note $\chi(k_z, k_z')$ is zero unless k_z and k_z' have the same parity. The $-(+)$ sign is used when n and n' are even (odd).

The density response function for our semiclassical infinite-barrier RPA model is given by (see, for example, Ref. 15)

$$\chi^n(k_z, k_z'; k_\parallel, \omega) = \frac{L}{2}\chi_B(\vec{k}, \omega)\delta_{k_z, \pm k_z'} - \frac{2k_\parallel}{k_\parallel^2 + k_z^2}\,\chi_B(\vec{k}, \omega)\,\frac{1}{D_{S,A}(\vec{k}_\parallel, \omega)}\,v(\vec{k}\,')\chi_B(\vec{k}\,', \omega) , \tag{4.5}$$

where $\vec{k} \equiv (\vec{k}_\parallel, k_z)$, $\vec{k}\,' \equiv (\vec{k}_\parallel, k_z')$, and

$$D_{S,A}(\vec{k}_\parallel, \omega) \equiv 1 + \frac{2}{L}\sum_{k_z}{}' \frac{k_\parallel}{k_\parallel^2 + k_z^2}\,\frac{1}{\epsilon_B(\vec{k}, \omega)} . \tag{4.6}$$

The sum in (4.6) is restricted to even (odd) values of k_z if k_z and k_z' in (4.5) are even (odd). The bulk RPA density response function is given by

$$\chi_B(\vec{k}, \omega) = \frac{\chi^0(\vec{k}, \omega)}{1 - v(\vec{k})\chi^0(\vec{k}, \omega)} \equiv \frac{\chi^0(\vec{k}, \omega)}{\epsilon_B(\vec{k}, \omega)} , \tag{4.7}$$

which also defines the bulk dielectric function which appears in (4.6). $\chi^0(\vec{k}, \omega)$ is the usual Lindhard function and $v(\vec{k})$ is the Fourier transform of the Coulomb interaction between the metal substrate electrons. Loosely speaking, one may view the second term on the right-hand side of (4.5) to be the surface-induced part of the density response function, especially in the $L \to \infty$ limit. In this case, (4.4) describes an adatom coupled to a semi-infinite metal whose surface is at $z = 0$. We remark that the density response function for a metal film of thickness L on a semi-infinite dielectric (from $z=L$ to ∞) may be obtained by specializing the expressions given in Sec. II of a paper by Harris and Griffin.[35] We do not discuss this case any further, although it might be the most relevant model in future studies of chemisorption on supported metal films.

Making use of (4.5), we find after a little algebra that

$$\begin{aligned}\frac{1}{L^2}\sum_{k_z,k'_z}\frac{\chi(k_z,k'_z;\vec{k}_\parallel,\omega)}{(k_z^2+k_\parallel^2)(k_z'^2+k_\parallel^2)}[1\mp\exp(-k_\parallel L)]^2\\ =\frac{1}{4\pi e^2k_\parallel}\Big[\tfrac{1}{2}D_S[1-\exp(-k_\parallel L)]^2-[1-\exp(-k_\parallel L)]+\tfrac{1}{2}D_A[1+\exp(-k_\parallel L)]^2-[1+\exp(-k_\parallel L)]\\ -\frac{2}{D_S}\left(\frac{1}{2}D_A-\frac{1}{1-\exp(-k_\parallel L)}\right)^2[1-\exp(-k_\parallel L)]^2-\frac{2}{D_A}\left(\frac{1}{2}D_A-\frac{1}{1+\exp(-k_\parallel L)}\right)^2[1+\exp(-k_\parallel L)]^2\Big]\,. \qquad (4.8)\end{aligned}$$

In the manipulations used to derive this, we have used the identity

$$\frac{1}{L}\sum_{k_z}{}'\frac{2k_\parallel}{k_z^2+k_\parallel^2}=\left(\frac{1\pm\exp(-k_\parallel L)}{1\mp\exp(-k_\parallel L)}\right),\quad \begin{array}{l}S\text{: upper sign,}\\ A\text{: lower sign.}\end{array} \qquad (4.9)$$

Using this in (4.4), we finally obtain

$$K(\omega)=(K_0e)^2\int_0^\infty dk_\parallel\exp(-2k_\parallel d)\left(1-\frac{1}{D_S(k_\parallel,\omega)}-\frac{1}{D_A(k_\parallel,\omega)}\right). \qquad (4.10)$$

In the half-space limit ($L\to\infty$), we have $D_S=D_A=D$, where

$$D(k_\parallel,\omega)=2+\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{2k_\parallel}{k_\parallel^2+k_z^2}\left(\frac{1-\epsilon_B(\vec{k}_\parallel,\omega)}{\epsilon_B(\vec{k},\omega)}\right). \qquad (4.11)$$

As discussed at length in the literature,[17] the zeros of $D_{S,A}(\vec{k}_\parallel,\omega)$ give the charge fluctuation spectrum of the metal slab, including bulk and surface plasmons. Thus the result in (4.10) shows in a very direct way how this spectrum determines the substrate-induced dynamic interaction $K(\omega)$ which enters in the adatom self-energy. If we had simply approximated $\chi''(k_z,k'_z)$ in (4.5) by the first (bulk) term on the right-hand side, then we would have obtained a completely different result, namely,

$$K_B(\omega)=\frac{K_0^2}{2}\int\frac{d\vec{k}}{(2\pi)^3}\exp(-2k_\parallel d)v^2(\vec{k})\chi_B(\vec{k},\omega)\,. \qquad (4.12)$$

In this approximation, $K(\omega)$ is determined by the zeros of $\epsilon_B(\vec{k},\omega)$ instead of the zeros of $D(\vec{k}_\parallel,\omega)$.

In the half-space limit, (4.10) is equivalent to the expression obtained by Harris and Jones[16] in their discussion of the dynamical image potential. It has also been derived by Datta and Newns[18] as well as Gadzuk[4] in their discussion of the XPS core hole spectra of adsorbed atoms. In terms of quantities introduced in these references, we have

$$R(k_\parallel,\omega)\equiv1-\frac{2}{D(k_\parallel,\omega)}=\frac{1-\epsilon_s(k_\parallel,\omega)}{1+\epsilon_s(k_\parallel,\omega)}\,, \qquad (4.13)$$

where

$$\frac{1}{\epsilon_s(k_\parallel,\omega)}\equiv D(k_\parallel,\omega)-1=\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{2k_\parallel}{k_\parallel^2+k_z^2}\frac{1}{\epsilon_B(\vec{k},\omega)}\,, \qquad (4.14)$$

with ϵ_s being sometimes referred to as the "surface dielectric function." It is clear from (4.14) that when the bulk dielectric function $\epsilon_B(\vec{k},\omega)$ depends on $\vec{k}$, $\epsilon_s(\vec{k}_\parallel,\omega)$ can no longer be approximated very well by $\epsilon_B(\vec{k}_\parallel,\omega)$. The results obtained by Gadzuk in several recent papers[4] on the relaxation energy of adsorbed atoms using this particular approximation have no basis except in so far as we can use

$$\lim_{k_\parallel\to0}\frac{k_\parallel}{(k_\parallel^2+k_z^2)}\simeq\pi\delta(k_z) \qquad (4.15)$$

in (4.14). Of course, we have $\epsilon_s(k_\parallel=0,\omega)=\epsilon_B(k_\parallel=0,\omega)$.

For later purposes, it is convenient to review some of the results obtained in the case of XPS from adsorbed atoms. Gumhalter and Newns[18] have generalized the work of Langreth[36] and others to obtain an expression for the spectral density of occupied core states $N_+(\epsilon)$ of an adsorbed atom. Expanding this, one finds (in our notation)

$$N_+(E)=e^{-\beta}\left(\delta(E-\Delta_r)+\frac{\mathrm{Im}K(\Delta_r-E)}{\pi(\Delta_r-E)^2}\theta(\Delta_r-E)\right), \qquad (4.16)$$

where $\theta(x)$ is the step function and

$$\beta \equiv \int_0^\infty \frac{d\omega}{\pi} \frac{\mathrm{Im}K(\omega)}{\omega^2}$$
$$\Delta_r \equiv \int_0^\infty \frac{d\omega}{\pi} \frac{\mathrm{Im}K(\omega)}{\omega} = -\tfrac{1}{2}K(\omega=0)\,. \tag{4.17}$$

The last equality in (4.17) follows from using a spectral representation and is quite general. Here $K(\omega)\equiv K(\omega - i0^+)$ and E is measured relative to the original occupied core orbital. We see that in this Born approximation, $N_+(\omega)$ exhibits a main resonance at the shifted frequency Δ_r (the so-called relaxation shift). The second term is a satellite structure. If we neglect electron-gas dispersion and set $\epsilon_B(\vec{k},\omega) = 1-\omega_p^2/\omega^2$, then (4.13) simplifies to ($\omega_{sp}=\omega_p/\sqrt{2}$)

$$R(k_\parallel, \omega) = \omega_{sp}^2/(\omega^2 - \omega_{sp}^2) \tag{4.18}$$

and hence from (4.10)

$$K(\omega) = K_0^2(e^2/2d)\omega_{sp}^2/(\omega^2-\omega_{sp}^2)\,. \tag{4.19}$$

In this limiting case, only the surface-plasmon mode is coupled to the adatom and (4.16) reduces to

$$N_+(E) = e^{-\beta}\{\delta(E-\Delta_r) + \beta\delta[E-(\Delta_r-\omega_{sp})]\}, \tag{4.20}$$

with

$$\beta = V_I/\omega_{sp}\,,\quad \Delta_r = V_I \equiv e^2/4d\,. \tag{4.21}$$

Thus we have a main resonance shifted up by the classical image-potential energy V_I and a surface-plasmon satellite shifted down from this "relaxed peak" by ω_{sp}. Using the more general formulas, one finds a whole series of surface plasmon satellites given by well-known formula[5]

$$N_+(E) = \sum_{n=0}^{\infty} (e^{-\beta}) \frac{\beta^n}{n!}\delta[E-(\Delta_r - n\omega_{sp})], \tag{4.22}$$

but usually $\beta \ll 1$.

When electron-gas dispersion is considered, $\mathrm{Im}K(\omega)$ has contributions from the bulk-plasmon continuum and the particle-hole continuum as well. Gadzuk[4] has discussed the relaxation shift Δ_r including such effects, which come in automatically when we use (4.10). The only analogous study of the satellite structure [second term in (4.16)] is by Datta and Newns.[19] However they only considered $K(\omega)$ for fairly large values of d (such as found in physisorption) and in this case the surface plasmon resonance still dominates. It is clear from the structure of $K(\omega)$ in (4.10) that the dominant contribution to $k_\parallel$ integral is from values $k_\parallel \lesssim d^{-1}$. Since electron gas dispersion [i.e., the k dependence of $\epsilon_B(\vec{k},\omega)$] only becomes significant for $k \gtrsim k_{FT}$ (Thomas-Fermi wave vector), the local approximation (4.19) can be expected to be adequate as long as $d \gtrsim k_{FT}^{-1}$. This is consistent with the numerical results of Datta and Newns.

We note that in the local approximation, we have $R(k_\parallel,\omega) = R(k_\parallel = 0, \omega)$ and thus $K(\omega)$ is given by (4.19). In fact, this result is exact to order d^{-1}. Contributions to $R(k_\parallel,\omega)$ which are linear in $k_\parallel$ will lead to a correction to (4.19) which is of order d^{-2}, and so on. Thus the first contributions to $K(\omega)$ from the bulk plasmon and particle-hole continuum will at least be of order d^{-2}.

If one is interested in the relaxation energy Δ_r given by (4.17), one only needs $K(\omega=0)$. At $\omega = 0$, one can use the Thomas-Fermi approximation

$$\epsilon_B(\vec{k}, \omega=0) \simeq 1 + k_{FT}^2/k^2\,,\quad k_{FT} = \sqrt{3}\omega_P/v_F \tag{4.23}$$

for wave vectors $|\vec{k}| < \bar{k}$. As a result, the integral in (4.11) is restricted to $|k_z| \leqslant k_c \equiv (\bar{k}^2 - k_\parallel^2)^{1/2}$ and we find[37]

$$D(k_\parallel, \omega=0) = 2 - \frac{2}{\pi}\arctan\frac{k_c}{k_\parallel} + \frac{k_\parallel}{(k_{FT}^2+k_\parallel^2)^{1/2}}\frac{2}{\pi}\arctan\frac{k_c}{(k_{FT}^2+k_\parallel^2)^{1/2}}\,. \tag{4.24}$$

An appropriate cutoff would be $\bar{k} \simeq k_{FT}$. Newns[38] (see also Gadzuk[4]) first worked out the relaxation shift Δ_r using (4.24) with $k_c \to \infty$, in which case it reduces to

$$D(k_\parallel, \omega=0) = 1 + k_\parallel/(k_{FT}^2 + k_\parallel^2)^{1/2}\,, \tag{4.25}$$

and thus we have

$$K(\omega=0) = -(K_0e^2)^2 \int_0^\infty dk_\parallel \exp(-2k_\parallel d)\left(\frac{Q-k_\parallel}{Q+k_\parallel}\right), \tag{4.26}$$

where $Q \equiv (k_\parallel^2 + k_{FT}^2)^{1/2}$. The leading-order correction of order d^{-2} to the relaxation shift is[4]

$$\Delta_r = -\tfrac{1}{2}K(\omega=0) = (e^2/4d)(1 - 1/k_{FT}d + \cdots)\,. \tag{4.27}$$

This result is equivalent to saying that the reference plane is at $z_0 = -k_{FT}^{-1}$. Clearly if $d \leqslant k_{FT}^{-1}$, then we must keep the cutoff $\bar{k}(\simeq k_{FT})$ in computing Δ_r.

For completeness, we also note that one may calculate $K(\omega)$ when the adatom is *inside* the metal surface. For $Z_a = +d_0$, we find in place of (4.4)

$$K(\omega)=(K_0e^2)^2\int d\vec{k}_\parallel\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_{-\infty}^{\infty}\frac{dk'_z}{2\pi}\times\frac{\chi''(k_z,k'_z;\vec{k}_\parallel,\omega)}{(k_\parallel^2+k_z^2)(k_\parallel^2+k_z'^2)}2[\exp(-k_\parallel d_0)-2\cos k_z d_0]\times[\exp(-k_\parallel d_0)-2\cos k'_z d_0],\tag{4.28}$$

where for simplicity we only give the half-space result ($L\to\infty$). As an illustration, in the Thomas-Fermi approximation based on (4.23), (4.5) reduces to

$$\chi(k_z,k'_z;k_\parallel,\omega=0)=-\frac{1}{4\pi e^2}\frac{k_{\mathrm{FT}}^2}{k^2+k_{\mathrm{FT}}^2}\times\left(\frac{L}{2}k^2\delta_{k_z,\pm k'_z}+\frac{2k_\parallel Q}{k_\parallel+Q}\frac{k_{\mathrm{FT}}^2}{k'^2+k_{\mathrm{FT}}^2}\right).\tag{4.29}$$

Using this in (4.28) we find, after some calculation,

$$K(\omega=0)=-(K_0e)^2\int_0^\infty dk_\parallel\left(\frac{Q-k_\parallel}{Q}-\frac{k_\parallel}{Q}\frac{Q-k_\parallel}{Q+k_\parallel}\times\exp(-2Qd_0)\right).\tag{4.30}$$

We note that for $d_0=0$, this agrees with (4.26) when $d=0$, as it should. The first term in the integrand, which is independent of the distance (d_0) the atom is inside the metal surface, gives the bulk relaxation energy. It follows immediately from (4.1) that for an atom in an infinite electron gas, $K(\omega)$ is given by

$$K_B(\omega)=K_0^2\int\frac{d\vec{k}}{(2\pi)^3}v^2(\vec{k})\chi_B(\vec{k},\omega)\tag{4.31}$$

and in the Thomas-Fermi approximation, this reduces to

$$K_B(\omega=0)=-\frac{2}{\pi}(K_0e)^2\int_0^\infty dk\frac{k_{\mathrm{FT}}^2}{k^2+k_{\mathrm{FT}}^2}=-(K_0e)^2k_{\mathrm{FT}}.\tag{4.32}$$

It can be verified that the first term in (4.30) involving $(Q-k_\parallel)/Q$ gives the same result as (4.32). Thus we have a simple estimate of surface-induced relaxation shift of a deep core state of an atom a distance d_0 inside a metal surface, namely

$$\Delta_r^{\mathrm{surf}}\simeq\left[\frac{e^2}{2}\int_0^\infty dk_\parallel\frac{k_\parallel}{Q}\left(\frac{Q-k_\parallel}{Q+k_\parallel}\right)\right]\exp(-2k_{\mathrm{FT}}d_0).\tag{4.33}$$

Combining (4.26) and (4.30), we have the Thomas-Fermi approximation to the energy of a stationary charge (K_0e) as a function of its position relative to the metal surface at $z=0$. For further discussion, we refer to recent work of Eguiluz,[39] who has obtained similar results based on a normal-mode analysis of the coupling of a charge to surface and bulk plasmons (the hydrodynamical model was used). His work shows how, as the charge moves from outside the metal to inside the metal, the surface-plasmon contribution becomes less important while the bulk-plasmon contribution becomes the dominant one.

V. CALCULATION OF ADATOM SPECTRAL DENSITY

We are now ready to compute the adatom density of states $N(\omega)$. The hopping self-energy is given by (3.15) while the Coulomb coupling self-energies to second order are given by (3.30) and (3.31). For simplicity, we shall evaluate these charge fluctuation self-energies using (4.19) for $K(\omega)$. That is to say, we only include coupling of the adatom to dispersionless surface plasmons.

Using the spectral theorem in (4.17), the direct self-energy in (3.30) is given by

$$\Sigma_{\alpha\alpha}^{(1)}=2\Delta_r(1-\langle\hat{n}_\alpha\rangle).\tag{5.1}$$

To leading order in d^{-1}, Δ_r is given by (4.21) and thus we have (we drop the α subscripts)

$$\Sigma^{(1)}=K_0^2(e^2/2d)(1-\langle\hat{n}_\alpha\rangle),\tag{5.2}$$

which is the image potential shift we would expect if the adatom had a net static charge $=e(1-\langle\hat{n}_\alpha\rangle)$. We shall not compute $\Sigma_{\alpha\alpha}^{(1)}$ self-consistently in our calculations. Moreover, in computing the exchange self-energy $\Sigma_{\alpha\beta}^{(2)\sigma}$ in (3.31), we shall use the auxiliary Hubbard Green's function $\hat{\mathcal{G}}_{\alpha\beta}^{\sigma}(\omega)$ given by the solution of (3.19). The only self-consistency we include is in the determination of the averages $\langle\hat{n}_{\beta\sigma}\rangle$ in (3.18).

In order to first obtain some qualitative understanding, we shall briefly study (3.31) with the single-pole approximation

$$\hat{\mathcal{G}}_{\alpha\beta}(\omega)=[1/(\omega-\hat{\epsilon}_\alpha)]\delta_{\alpha\beta},\tag{5.3}$$

where $\hat{\epsilon}_\alpha$ describes the atomic energy levels renormalized to include the shift due to the hopping self-energy. With (5.3) and (4.19), the exchange self-energy reduces to $\Sigma_{\alpha\beta}^{(2)\sigma}(\omega)=\Sigma_{\alpha\alpha}^{(2)}(\omega)\delta_{\alpha\beta}$, with

$$\Sigma_{\alpha\alpha}^{(2)}(\omega)=K_0^2\left(\frac{e^2}{4d}\right)\frac{\omega_{sp}}{\omega-\hat{\epsilon}_\alpha-\alpha\omega_{sp}}.\tag{5.4}$$

We have assumed that $\hat{\epsilon}_-<0$ and $\hat{\epsilon}_+>0$, with the Fermi energy set at 0. The Hubbard Green's function is then simply ($\Sigma_{\alpha\alpha}=\Sigma^{(1)}+\Sigma_{\alpha\alpha}^{(2)}$),

$$\mathcal{G}^{\sigma}_{\alpha\beta}(\omega) = \langle \hat{n}_{\beta\sigma}\rangle \delta_{\alpha\beta}/[\omega - \hat{\epsilon}_{\alpha} - \Sigma_{\alpha\alpha}(\omega)] . \tag{5.5}$$

The poles are given by the solutions Ω of

$$x_{\alpha} - \Sigma^{(1)} = V_I[\omega_{sp}/(x_{\alpha} - \alpha\omega_{sp})] , \tag{5.6}$$

where $x_{\alpha} \equiv \Omega - \hat{\epsilon}_{\alpha}$. One has two solutions for each α,

$$\Omega_{\alpha} = \hat{\epsilon}_{\alpha} + \tfrac{1}{2}(\Sigma^{(1)} + \alpha\omega_{sp}) \pm \tfrac{1}{2}[(\Sigma^{(1)} - \alpha\omega_{sp})^2 + 4V_I\omega_{sp}]^{1/2} . \tag{5.7}$$

Making use of the fact that $V_I \ll \omega_{sp}$, we have

$$\begin{aligned} &\Omega^{(1)}_{-} \simeq \hat{\epsilon}_{-} + \Sigma^{(1)} + V_I , \quad \Omega^{(2)}_{-} = \hat{\epsilon}_{-} - (\omega_{sp} + V_I) , \\ &\Omega^{(1)}_{+} \simeq \hat{\epsilon}_{+} + \Sigma^{(1)} - V_I , \quad \Omega^{(2)}_{+} = \hat{\epsilon}_{+} + (\omega_{sp} + V_I) . \end{aligned} \tag{5.8}$$

Thus both the ionization level ($\alpha = -$) and the affinity level ($\alpha = +$) are split into two peaks. The relative weights of the two resonances is

$$W(\Omega^{(2)}_{\alpha})/W(\Omega^{(1)}_{\alpha}) \simeq \beta = V_I/\omega_{sp} \ll 1 . \tag{5.9}$$

The peak near the ionization level $\hat{\epsilon}_{-}$ which has the largest weight is shifted *up* by an amount $V_I + \Sigma^{(1)}$. It corresponds to the "relaxed elastic" or "zero-plasmon" peak of the core level in XPS studies discussed in Sec. IV. A second peak of relative weight (V_I/ω_{sp}) is shifted down by $(\omega_{sp} + V_I)$ and is the "shake-up" or "one-plasmon" satellite. Similarly, the renormalized affinity level $\hat{\epsilon}_{+}$ is split into two peaks. The one with largest weight is shifted down by $V_I - \Sigma^{(1)}$ and is the analog of the relaxed "valence" level in core level XPS. The surface plasmon satellite is shifted up from $\hat{\epsilon}_{+}$ by $(\omega_{sp} + V_I)$. If one of the main resonances $(\Omega^{(1)}_{-}, \Omega^{(1)}_{+})$ crossed the Fermi level $(\epsilon_F = 0)$, of course, there will be a net charge transfer between adatom and substrate. We have not considered this possibility here, although it is a topic of some considerable interest[6-8] in connection with XPS studies.

To summarize, we have seen that if we start with a adatom Green's function with sharp resonances at $\hat{\epsilon}_{-} < 0$ and $\hat{\epsilon}_{+} > 0$, the renormalized atomic peaks occur at (assuming $\omega_{sp} \gg V_I$)

$$\begin{aligned} &E_{-} = \hat{\epsilon}_{-} + 2V_I(1 - \langle \hat{n}_a \rangle) + V_I , \\ &E_{+} = \hat{\epsilon}_{+} + 2V_I(1 - \langle \hat{n}_a \rangle) - V_I . \end{aligned} \tag{5.10}$$

These results are often described by saying that the Coulomb interaction K_{ai} between the metal and adatom allows the substrate electron gas to "screen" the bare adatom Coulomb repulsion U,

$$U \to U_{\mathrm{eff}} = U - 2V_I . \tag{5.11}$$

It is quite gratifying that we are able to obtain results such as (5.10) and (5.11) as the first approximation to a general theory of the effect of substrate charge fluctuations. The only comparable microscopic calculation given in the literature is that of Newns and co-workers[19,20] but they only considered a *single* sharp level ($U \to \infty$). Another nice feature of our calculation is how surface plasmon satellites automatically arise. Their relative weight [compared to the main peaks given by (5.10)] is small. However, the shifts are large ($\sim\omega_{sp}$), and it is important to take ionization level surface-plasmon satellite into account when one calculates the effect of substrate charge fluctuations on the total chemisorption energy. As we shall discuss in Sec. VI, the large surface plasmon downward shift exactly cancels the small upward shift of the main ionization peak.

While (5.5) might be appropriate to deep core states as well as physisorbed atoms, it is clearly not very adequate for the valence electrons involved in chemisorption, where the hopping self-energy gives rise to an adatom propagator with a fairly complicated spectral density (see Sec. III). We shall now discuss some numerical results based on calculating $\Sigma^{(2)}_{\alpha\beta}(\omega)$ using the BS approximation[10] for $\hat{\mathcal{G}}_{\alpha\beta}(\omega)$. We have ignored $\Sigma^{(1)}$ in these calculations. This is justified if $\langle n_{a\uparrow}\rangle = \langle n_{a\downarrow}\rangle \simeq \frac{1}{2}$ or $\langle n_a \rangle = 1$ (no net charge transfer). The resulting adatom Green's functions were found to be consistent with this assumption (i.e., $\langle n_a \rangle \simeq 1$ to within approximately 10%).

In Figs. 4 and 5, we show the effect of the surface charge fluctuations on the adatom density of states $N(\omega)$ given in Figs. 2 and 3. We use the same model parameters given in Sec. III. The surface-plasmon energy was taken to be $\omega_{sp} = 8$ eV. The strength of the Coulomb coupling is conveniently parametrized by V_I. In Fig. 4 ($V = 3$ eV), we have only one well-defined peak below (or above) $\epsilon_F = 0$, associated with the original atomic level ϵ_a (or $\epsilon_a + U$). The resulting relaxation shifts and surface-plasmon satellites are in accordance with the results discussed above, based on (5.3). However, we find for larger V_I, the relaxation shift is considerably less than V_I, although the surface-plasmon satellites still occur at $\pm(\omega_{sp} + V_I)$ away from the original resonance [compare with (5.8)]. The two broad resonances just outside the d band also are found to exhibit weak surface plasmon satellite structures. The kinks at $\omega \simeq \pm 8$ eV are a result of the broad peak close to $\omega = 0$. For $V_I = 3$ eV, the shoulder on the main line at around $\omega \simeq -12.5$ eVis a satellite of the resonance at $\omega \simeq -4.5$ eV. We also call attention to the large loss of intensity of the renormalized ionization peak compared to renormalized affinity level.

In the case shown in Fig. 5, V_I is large enough that extra resonances have split off from the d band (denoted by B and C), and these also exhibit

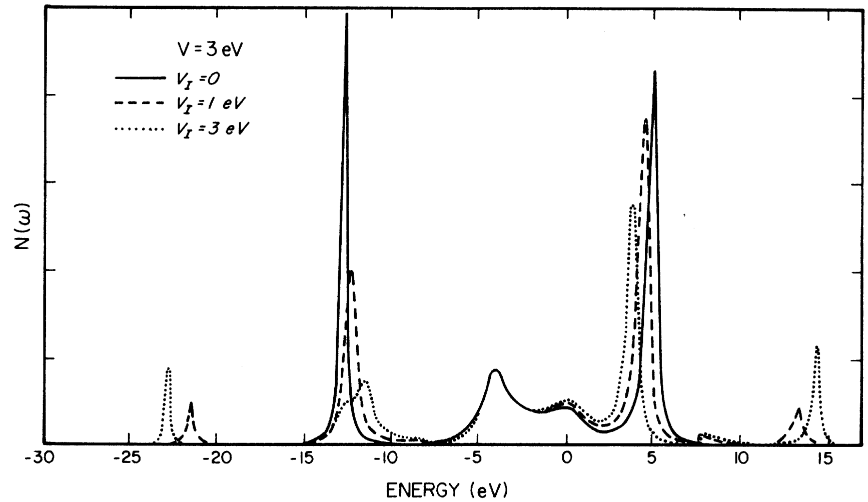

FIG. 4. Plot of the adatom density of states $N(\omega)$ for three different values of the Coulomb coupling between adatom and metal (parametrized in terms of the image potential V_I). The extra peaks are surface-plasmon satellites.

surface plasmon satellites (denoted by B' and C'). In this connection, it is clear that if we calculated $\Sigma^{(2)}_{\alpha\alpha}(\omega)$ self-consistently with the renormalized adatom Green's function, one would find that the satellites would have satellites. Our final iterated solution would have a series of surface plasmon satellites approximately at $-n\omega_{sp}(n=1,2,3,\ldots)$ below (above) the ionization (affinity) levels $\epsilon_-(\epsilon_+)$. The weight of the nth satellite would also be roughly given by β^n, where $\beta = V_I/\omega_{sp} \ll 1$. Of course, a proper theory of these satellites requires more diagrams than the subset summed by using our self-consistent Born approximation (3.31) for $\Sigma^{(2)}(\omega)$. We refer to the work of Langreth[36] as well as Gumhalter and Newns[18] for further discussion.

The results in Figs. 4 and 5 are for the case of a narrow d band which is almost filled (such as nickel). In order to give further insight into the effect of surface plasmons, in Fig. 6 we give some results using a band model more appropriate to something like tungsten. The band is almost half-filled and has a width $2W = 9$ eV. The band center is at -5.3 eV relative to the vacuum.

VI. EFFECT OF SUBSTRATE CHARGE FLUCTUATIONS ON THE CHEMISORPTION ENERGY

In Sec. V, we have seen the strong effect substrate charge fluctuations have on the adatom spectral density. Here we shall show that, in spite of this, these charge fluctuations have little

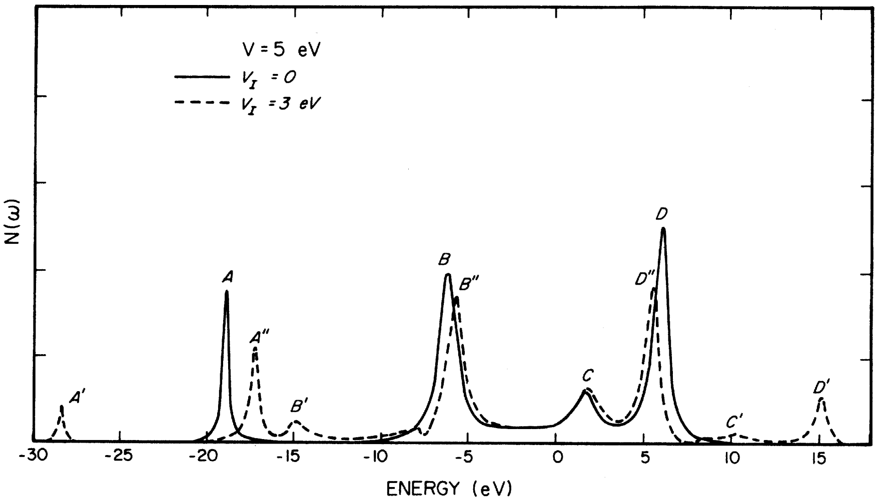

FIG. 5. Same as Fig. 4, except that the hopping strength V is larger.

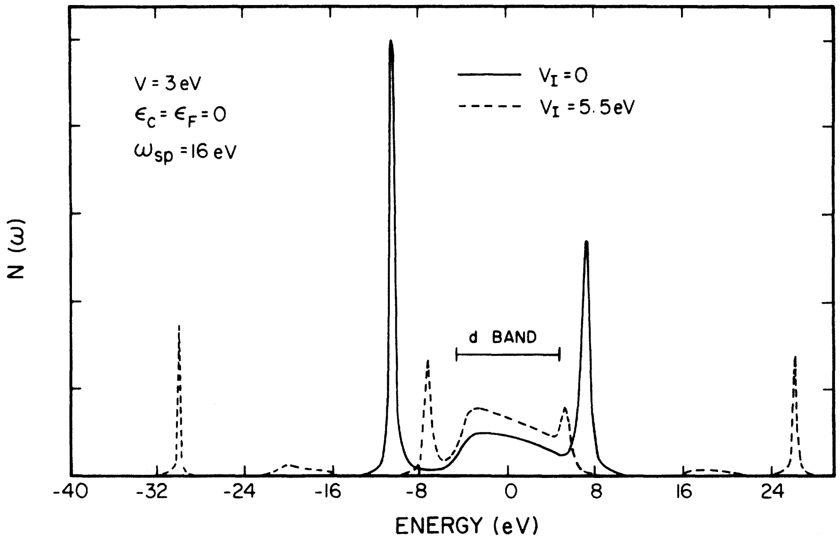

FIG. 6. Spectral density of H atom chemisorbed on a metal with a wide *d* band. Results are shown for two values of the image potential V_I, which is a measure of the coupling to the surface plasmons (whose energy is taken to be 16 eV).

effect on the total chemisorption energy. This result may be viewed as a form of Lundqvist's compensation sum rule.[21,36]

The extra contribution (ΔE) to the chemisorption energy will be calculated by using the coupling constant integration technique

$$\Delta E = \int_0^1 \frac{d\lambda}{\lambda} \langle K_{ma} \rangle_\lambda$$

$$= \sum_i \int_0^1 d\lambda K_{ai} \langle \hat{n}_i (\hat{n}_a - 1) \rangle_\lambda \,. \tag{6.1}$$

Here $\langle \cdots \rangle_\lambda$ means one is to calculate the expectation value of the operators with respect to the exact ground state when the adatom-metal Coulomb interaction λK_{ai}. The mixed adatom-metal electron response functions in (6.1) may be obtained using the functional-derivative technique used in Secs. II and III. Using (2.7), we have

$$\langle K_{ma} \rangle = \langle K_{ma} \rangle^{(1)}$$

$$+ \frac{1}{-i\beta} \sum_{i,\sigma'} K_{ai} \left(\frac{\delta}{\delta X_i^\sigma(\bar{\tau})} + \frac{\delta}{\delta X_i^{-\sigma}(\bar{\tau})} \right) G_{aa}^{\sigma'}(\bar{\tau}, \bar{\tau}^+) \,, \tag{6.2}$$

where

$$\langle K_{ma} \rangle^{(1)} \equiv \sum_{i,\sigma} K_{ai} [-iG_{ii}(\tau, \tau^\dagger)][-iG_{aa}^\sigma(\tau, \tau^\dagger)]$$

$$- \sum_i K_{ai} [-iG_{ii}(\tau, \tau^\dagger)]$$

$$= \sum_i K_{ai} \langle \hat{n}_i \rangle (\langle \hat{n}_a \rangle - 1) \,. \tag{6.3}$$

Using the results of Sec. III, we have

$$\frac{\delta G_{aa}^{\sigma'}(\tau, \tau^\dagger)}{\delta X_i^\sigma(\tau)} = \sum_{\substack{\alpha,\beta \\ \gamma,\delta}} \hat{\mathcal{G}}_{\alpha\beta}^{\sigma'}(\tau, \bar{\tau}_1) \frac{\delta \hat{\Sigma}_{\beta\gamma}^{\sigma'}(\bar{\tau}_1, \bar{\tau}_2)}{\delta X_i^\sigma(\tau)}$$

$$\times \hat{\mathcal{G}}_{\gamma\delta}^{\sigma'}(\bar{\tau}_2, \tau^\dagger) \langle n_{\delta\sigma'} \rangle \,. \tag{6.4}$$

Here we have neglected the functional derivative of the density $\langle n_{\delta\sigma'} \rangle$, since we are only interested in evaluating (6.4) to lowest order in K. In view of this, it is also sufficient to use the first-order self-energy

$$\hat{\Sigma}_{\beta\gamma}^{\sigma'}(\tau_1, \tau_2) \simeq -i \sum_{j,\sigma} K_{aj} G_{jj}^{\sigma'}(\tau_1, \tau_1^\dagger) \delta(\tau_1 - \tau_2) \delta_{\beta\gamma} \tag{6.5}$$

and thus (6.4) reduces to

$$\sum_\sigma \frac{\delta G_{aa}^{\sigma'}(\tau, \tau^\dagger)}{\delta X_i^\sigma(\tau)} = \sum_{\substack{j \\ \alpha,\beta,\delta}} \mathcal{G}_{\alpha\beta}^{\sigma'}(\tau, \bar{\tau}_1) K_{aj} \chi_{ij}^n(\tau, \bar{\tau}_1)$$

$$\times \hat{\mathcal{G}}_{\beta\delta}^{\sigma'}(\bar{\tau}_1, \tau^\dagger) \langle n_{\delta\sigma'} \rangle \,. \tag{6.6}$$

Combining all these results and Fourier transforming to imaginary frequencies, we obtain, finally,

$$\langle K_{ma} \rangle_\lambda^{(2)} = \frac{1}{\beta} \sum_{\omega_n} \sum_{\substack{\alpha,\beta \\ \delta,\sigma}} \lambda^2 \Sigma_{\alpha\beta}^{(2)\sigma}(i\omega_n) \hat{\mathcal{G}}_{\beta\delta}^\sigma(i\omega_n) \langle n_{\delta\sigma} \rangle \,, \tag{6.7}$$

where

$$\Sigma_{\alpha\beta}^{(2)\sigma}(i\omega_n) = \sum_{i,j,\omega_l} K_{ai} K_{aj} \chi_{ij}^n(i\omega_l) \mathcal{G}^\sigma{}_{\alpha\beta}(i\omega_n - i\omega_l) \,, \tag{6.8}$$

the sum over ω_l being over Bose-Matsubara frequencies.

Recalling (2.29), we see that (6.3) is given by

$$\langle K_{ma}\rangle_\lambda^{(1)} = \lambda^2 \sum_{i,j} K_{ai}K_{aj}\chi^n_{ij}(\omega=0)(\langle\hat{n}_a\rangle - 1)^2$$
$$= \lambda^2\Sigma^{(1)}(\langle\hat{n}_a\rangle - 1) \tag{6.9}$$

and hence it vanishes if there is no charge transfer, $\langle\hat{n}_a\rangle = 1$. In evaluating the exchange contribution (6.7) makes to the chemisorption energy, we shall assume that the direct contribution to the self-energy is zero. We shall approximate $\Sigma^{(2)}_{\alpha\alpha}(i\omega_n)$ by (5.4) and use

$$\hat{\mathcal{G}}_{\alpha\beta}(i\omega_n) = \delta_{\alpha\beta}/[i\omega_n - \hat{\epsilon}_\alpha - \Sigma^{(2)}_{\alpha\alpha}(i\omega_n)] \tag{6.10}$$

for the diagonal elements of the auxiliary Hubbard Green's function in (6.7). Finally we shall ignore any dependence of $\langle\hat{n}_{\alpha\sigma}\rangle$ on the coupling constant λ. The exchange contribution to the chemisorption energy is thus

$$\Delta E^{(2)} = -\frac{1}{\beta}\sum_{\omega_n,\alpha,\sigma}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{\lambda^2\Sigma^{(2)}_{\alpha\alpha}(i\omega_n)\langle\hat{n}_{\alpha\sigma}\rangle}{i\omega_n - \hat{\epsilon}_\alpha - \lambda^2\Sigma^{(2)}_{\alpha\alpha}(i\omega_n)} \tag{6.11}$$

$$= -\frac{1}{2\beta}\sum_{\omega_n,\alpha,\sigma}\{\ln[i\omega_n - \hat{\epsilon}_\alpha - \Sigma^{(2)}_{\alpha\alpha}(i\omega_n)] - \ln(i\omega_n - \hat{\epsilon}_\alpha)\}\langle\hat{n}_{\alpha\sigma}\rangle\,. \tag{6.12}$$

Using standard methods,[25] we can convert the Matsubara frequency sum over ω_n to a contour integral

$$\Delta E^{(2)} = -\frac{1}{2}\sum_{\alpha,\sigma}\oint_c \frac{d\omega}{2\pi i}\left(\frac{1}{e^{\beta\omega}+1}\right)\{\ln[\omega - \hat{\epsilon}_\alpha - \Sigma^{(2)}_{\alpha\alpha}(\omega)] - \ln(\omega - \hat{\epsilon}_\alpha)\}\langle n_{\alpha\sigma}\rangle\,. \tag{6.13}$$

The contour c encloses the imaginary frequency axis, which we deform to c' which encloses the real frequency axis. In the limit of zero temperature, the Fermi factor makes the integrand vanish for positive frequencies (recall that $\epsilon_F = 0$) and we are left with a clockwise contour c'' around the negative frequency axis. Integrating by parts, we find

$$\Delta E^{(2)} = -\frac{1}{2}\sum_{\alpha,\sigma}\oint_{c''}\frac{d\omega}{2\pi i}\,\omega\left[\frac{1}{\omega - \hat{\epsilon}_\alpha - \Sigma^{(2)}_{\alpha\alpha}(\omega)}\times\left(1 - \frac{\partial\Sigma^{(2)}_{\alpha\alpha}(\omega)}{\partial\omega}\right) - \frac{1}{\omega - \hat{\epsilon}_\alpha}\right]\langle n_{\alpha\sigma}\rangle\,. \tag{6.14}$$

Using Cauchy's theorem to pick up the contribution of the poles (for a similar calculation, see Ref. 17), we obtain

$$\Delta E^{(2)} = \frac{1}{2}\sum_{\alpha,\sigma}{}' (\Omega_\alpha - \Omega^0_\alpha - \hat{\epsilon}_\alpha)\langle n_{\alpha\sigma}\rangle\,. \tag{6.15}$$

Here Ω_α is a pole of $\hat{\mathcal{G}}^\sigma_{\alpha\alpha}(\omega)$:

$$\Omega_\alpha - \epsilon_\alpha - \Sigma^{(2)}_{\alpha\alpha}(\Omega_\alpha) = 0\,, \tag{6.16}$$

while Ω^0_α is a pole of $\Sigma^{(2)}_{\alpha\alpha}(\omega)$:

$$\Sigma^{(2)}_{\alpha\alpha}(\Omega^0) = \infty\,. \tag{6.17}$$

The prime on the summation in (6.15) denotes the fact that the contour in (6.14) only includes states ($\Omega_\alpha, \Omega^0_\alpha$, and $\hat{\epsilon}_\alpha$) which are occupied (i.e., less than the Fermi energy).

In the surface-plasmon approximation discussed in Sec. V, we have

$$\Sigma^{(2)}_{\alpha\alpha}(\omega) = V_I\omega_{sp}/(\omega - \hat{\epsilon}_\alpha - \alpha\omega_{sp})\,. \tag{6.18}$$

Clearly, we have

$$\Omega^0_\alpha = \hat{\epsilon}_\alpha + \alpha\omega_{sp}\,, \tag{6.19}$$

while Ω_α is given by (5.7). We recall from the discussion in Sec. V that for each α, there are two solutions, corresponding to a "relaxed" main line and a surface-plasmon satellite. We assume that $\hat{\epsilon}_+$, Ω_+, and Ω^0_+ are all above the Fermi energy (i.e., positive) and hence are not occupied. Using (5.7) and (6.19) in (6.15), we obtain, finally,

$$\Delta E^{(2)} = \frac{1}{2}\sum_\sigma\langle n_{-\sigma}\rangle(\Omega^{(1)}_- + \Omega^{(2)}_- - \Omega^0_- - \hat{\epsilon}_-)$$
$$= (2 - \langle\hat{n}_a\rangle)[2\hat{\epsilon}_- - \omega_{sp} - (\hat{\epsilon}_- - \omega_{sp}) - \hat{\epsilon}_-] = 0\,. \tag{6.20}$$

We conclude that while the exchange self-energy in (6.8) gives rise to considerable changes in the adatom energy spectrum (see Sec. V), it has no *net* effect on the total chemisorption energy. This is on the assumption, we emphasize, that none of the energy levels cross the Fermi level and there is no charge transfer.

Turning to the direct contribution in (6.9), we can easily carry out the λ integration if we ignore any λ dependence of $\langle\hat{n}_a\rangle$, with the result

$$\Delta E^{(1)} = \tfrac{1}{2}K(\omega=0)(\langle\hat{n}_a\rangle - 1)^2 = -V_I(\langle\hat{n}_a\rangle - 1)^2\,. \tag{6.21}$$

As expected, we see that the effect of the surface charge fluctuations is to increase the chemisorption binding energy.

We emphasize that, if the effect of the renormalization is to cause one of the resonances to cross the Fermi level so that levels become filled (or empty), then the whole question of charge transfer must be treated very carefully and self-consistently.[6] We have not considered this possibility, but our calculations could be generalized to do so. Such effects have been considered recently in connection with core-level spectra[7,8,40] using a model-Hamiltonian approach.

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APPENDIX

In our numerical calculations, we have evaluated the hopping self-energy in (2.34) including broadening $\omega \rightarrow \omega - i/\tau$. In the semielliptical one-dimensional model used in this paper, we have[10]

$$\Gamma(\omega) = (V^2/W^2)\{\omega' - i/\tau - [(\omega' - i/\tau)^2 - W^2]^{1/2}\}. \tag{A1}$$

Here $2W$ is the bandwidth and $\omega' \equiv \omega + \epsilon_F - \epsilon_c$, where ω is the energy measured relative to the Fermi energy ϵ_F and ϵ_c is the band center. More explicitly, we have

$$\mathrm{Re}\Gamma(\omega) = \begin{cases} \omega' - [\tfrac{1}{2}(r-x)]^{1/2}, & 0 < \omega' < W', \\ \omega' + [\tfrac{1}{2}(r-x)]^{1/2}, & -W' < \omega' < 0, \\ \omega' - [\tfrac{1}{2}(r+x)]^{1/2}, & \omega' > W', \\ \omega' + [\tfrac{1}{2}(r+x)]^{1/2}, & \omega' < -W', \end{cases} \tag{A2}$$

and

$$\mathrm{Im}\Gamma(\omega) = \begin{cases} -1/\tau + [\tfrac{1}{2}(r+x)]^{1/2}, & |\omega'| < W', \\ -1/\tau + [\tfrac{1}{2}(r-x)]^{1/2}, & |\omega'| > W', \end{cases} \tag{A3}$$

where

$$x \equiv |\omega'^2 - W'|^2, \qquad r \equiv +[x^2 + (2\omega'/\tau)^2]^{1/2} \tag{A4}$$

and the effective half bandwidth is

$$W' \equiv +[W^2 + (1/\tau)^2]^{1/2}. \tag{A5}$$

In our numerical calculations, we took $1/\tau = 1$ eV.

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*Present address: Dept. of Chemistry, University of Regensburg, Regensburg 8400, W. Germany.

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