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## Effect of the Image Force in Chemisorption

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An important contribution towards the well-known ionization of alkali atoms chemisorbed at low coverages on transition metal surfaces comes from the upward shift in the alkali valence level due to the image force. The Hartree-Fock approximation for this upward shift, in which the image of the adatom electron cloud is assumed static, may differ by up to a factor of two from that using the result that the self-image energy of an electron at a distance  $d$  from a metal surface is given by  $v = e^2/4d$ . The resolution of this problem depends on the lifetime of an electron in the adatom orbital and the dielectric response of the metal surface. A simple model Hamiltonian is put forward which includes these effects, and which is solved in limiting cases. In particular it is found that the HF approximation should overestimate the upward shift in the case of a substrate such as tungsten. Possible implications for the screening of the Coulomb interaction between electrons in an adatom orbital are discussed.

### §1. Introduction

The classical image energy of a charge  $q$  at a distance  $d$  outside a plane conducting surface is a quantity  $q^2/4d$  defined as the energy required to remove the charge to  $d = \infty$ . It is well known that such a term plays an important role in stabilising cationic adsorbed species, such as alkali atoms on transition metal surfaces,<sup>1)</sup> and is included in self-consistent theories of alkali chemisorption.<sup>2,3)</sup> The image effect may also influence other chemisorbed systems. In the case of adsorption, where  $d$  is microscopic, the simple classical formula may be used as a first approximation for adsorbed species of relatively large radius such as adsorbed caesium provided  $d$  is interpreted as the distance from an effective 'image plane'.

No further conceptual difficulty in calculating the image energy arises when  $q$  is a good quantum number. In practice, however, the valence levels of the alkali adsorbates are broadened by interaction with the substrate and are partially filled to the substrate Fermi-level,<sup>2,3)</sup> giving in effect a fluctuating electronic contribution to the charge  $q$ . If the electron did not interact with its own image, the valence level of an alkali cation at a distance  $d$  from a surface would be shifted by  $e^2/2d$  due to the electron-cation image repulsion. The effective valence level would be

$$\varepsilon_s = \phi - I + e^2/2d \quad (1)$$

relative to the substrate Fermi-level, where  $\phi$

is the substrate work function and  $I$  the valence ionisation potential of the alkali adsorbate. Let  $\langle n_s \rangle$  be the expectation value for the number of electrons in the alkali valence orbital. This would produce an average image charge of  $\langle n_s \rangle e$ , and, if this image were a completely static quantity, the true valence level would be

$$\varepsilon_{\text{eff}} = \phi - I + \frac{e^2}{2d}(1 - \langle n_s \rangle). \quad (2)$$

On the other hand, we might argue that when the electron is in the valence orbital it would experience the self-image energy  $-e^2/4d$  giving an effective level

$$\varepsilon_{\text{eff}} = \phi - I + e^2/4d. \quad (3)$$

This result would seem to imply that the image charge responds instantaneously to the fluctuation in the number of electrons in the adatom orbital. Both results show the familiar upward shift<sup>2,3)</sup> in the energy level of the adatom tending to ionise it but the quantitative difference is significant. Similar difficulties occur in calculating the total energy of the system.

At the present time measurements of changes in the electronic density of states in energy associated with an adsorbed species are becoming possible by photoemission,<sup>4)</sup> ion neutralisation,<sup>5)</sup> field emission<sup>6)</sup> and other techniques. Energy shifts of the order of  $e^2/4d$  are of the same order as the energy spacing on which structure is measured and particularly important where relatively narrow adsorbate energy levels are concerned. It would therefore

seem to be of interest to investigate the apparently contradictory results (2) and (3) from a more fundamental standpoint. In the following we shall be considering an alkali adsorbate in particular, although a wider application of our approach is possible.

## §2. Model Hamiltonian

The interaction of a classical time-varying charge  $en(t)$ , fixed at a distance  $d$  outside a solid surface, with its image may be described in a conventional approximation<sup>7)</sup> by a Hamiltonian of the type

$$H = \sum_{\mathbf{K}} \omega_{\mathbf{K}} b_{\mathbf{K}}^{\dagger} b_{\mathbf{K}} + n \sum_{\mathbf{K}} V_{\mathbf{K}} (b_{\mathbf{K}}^{\dagger} + b_{\mathbf{K}}). \quad (4)$$

Here  $b_{\mathbf{K}}^{\dagger}$ ,  $b_{\mathbf{K}}$  are boson creation and destruction operators for a surface plasmon of wave vector  $\mathbf{K}$  parallel to the surface, and frequency  $\omega_{\mathbf{K}}$ , and the  $V_{\mathbf{K}}$  (chosen to be real) are charge-surface plasmon coupling constants. The bulk plasmons do not interact with an external charge, and are therefore neglected in (4), as also are electron-hole excitations, the latter being discussed somewhat further below. If we make the additional approximation that  $\omega_{\mathbf{K}} = \omega_0$  is independent of  $\mathbf{K}$ , then (4) may be rewritten in the slightly simpler form

$$H = H_1 + H_2$$

where

$$H_1 = b^{\dagger} b \omega_0 + n \lambda [b^{\dagger} + b] \quad (5)$$

with

$$b = \lambda^{-1} \sum_{\mathbf{K}} V_{\mathbf{K}} b_{\mathbf{K}}; \quad \lambda^2 = \sum_{\mathbf{K}} V_{\mathbf{K}}^2,$$

and  $H_2$  does not depend on  $n$ . Eq. (5) describes the interaction of the charge  $en(t)$  with a single harmonic oscillator of frequency  $\omega_0$ .

In the present problem the charge  $en$  is an electron coupled quantum-mechanically to the solid surface. Following earlier work on model Hamiltonians in chemisorption<sup>8)</sup> this effect may be brought in through the Hamiltonian

$$H = \varepsilon_s n_s + \sum_k \varepsilon_k n_k + \sum_k [V_{sk} c_s^{\dagger} c_k + \text{H.c.}] + \omega_0 b^{\dagger} b + \lambda n_s (b^{\dagger} + b). \quad (6)$$

Here  $c_s^{\dagger}$  and  $c_k^{\dagger}$  are Fermion creation operators for the adatom valence level  $|s\rangle$  of energy  $\varepsilon_s$  and the eigenstates  $|k\rangle$  of the semi-infinite metal of energy  $\varepsilon_k$  respectively.  $n_s = c_s^{\dagger} c_s$  is the number operator for electrons in the adatom

orbital. The time dependence of the electronic charge represented by  $en_s$  on the adatom is brought in through the tunneling matrix element  $V_{sk} = \langle s|V|k\rangle$ , where  $V$  is an effective perturbation due to bringing the atom up to the surface; the term in  $H$  proportional to  $V_{sk}$  represents transfer of an electron from metal to adatom.

It should be noted that in contrast to previous work spin has been ignored in eq. (6), along with the Coulomb interaction  $U^{8,9)}$  between electrons of opposite spin in the adatom orbital. In a case such as that of an alkali atom adsorbed at low coverage on a transition metal surface it is generally the case that  $\langle n_s \rangle$ , the average occupation of the adatom orbital, is fairly small.<sup>2,3,10)</sup> Hence the probability of interaction between electrons of opposite spin should be small compared to that between an electron and its own image, and it is therefore believed that (6) should give a reasonable description of the latter effect under these conditions.

The unperturbed adatom level  $\varepsilon_s$  is to be given by (1) relative to the substrate Fermi level, which will be taken as the zero of energy in the following. Thus the effect of the unchanging adatom core charge is already taken into account in (6), the interaction term describing only the interaction of the electron with its own image.

The plasmon-electron interaction term can be removed explicitly from the Hamiltonian (6) by a canonical transformation. The operator that effects this is

$$U_s = \exp \left[ -\frac{\lambda}{\omega_0} (b^{\dagger} - b) c_s^{\dagger} c_s \right] \quad (7)$$

and the transformed Hamiltonian,  $H' = U_s^{-1} H U_s$ , is given by

$$H' = (\varepsilon_s - \lambda^2 / \omega_0) c_s^{\dagger} c_s + \omega_0 b^{\dagger} b + \sum_k \varepsilon_k c_k^{\dagger} c_k + \sum_k \left[ V_{sk} c_k^{\dagger} c_s \exp \left\{ -\frac{\lambda}{\omega_0} (b^{\dagger} - b) \right\} + V_{ks} c_s^{\dagger} c_k \exp \left\{ \frac{\lambda}{\omega_0} (b^{\dagger} - b) \right\} \right] \quad (8)$$

The modification to the hopping term between adatom and metal is due to the 'kick' the plasmon oscillator receives whenever the occupation of the adatom orbital changes which can cause any number of plasmons to be

created or absorbed.

For  $V_{sk}=0$  the adatom level is well defined and shifted from  $\varepsilon_s$  to  $\varepsilon_s - \lambda^2/\omega_0$  by the surface plasmon screening. This shift is the interaction energy of the adatom electron with its induced image charge, so

$$\lambda^2/\omega_0 = e^2/4d \quad (=v). \quad (9)$$

It will be convenient for later discussion to denote this by one parameter  $v = e^2/4d = \lambda^2/\omega_0$ .

### §3. Electron Green's Function for Isolated Adatom

As a basis for understanding the behaviour of this model we calculate the one-electron Green's function  $G_s(t, t')$  for the adatom. The time-dependent thermal Green's function, defined in the standard way at temperature  $T_0$ , is

$$G_s(t, t') = -i \frac{\text{Tr}\{T c_s^+(t') c_s(t) e^{-\beta H}\}}{\text{Tr}\{e^{-\beta H}\}} \quad (10)$$

where  $T$  is the usual time ordering operator and  $\beta = 1/kT_0$ . The trace is taken over a complete set of oscillator and many electron states, and  $c_s(t)$ ,  $c_s^+(t')$  are operators for the adatom orbital in the Heisenberg representation,

$$i.e. \quad c_s(t) = e^{iHt} c_s e^{-iHt}. \quad (11)$$

We may calculate the Green's function with respect to the canonically transformed Hamiltonian  $H'$  by substituting  $H = U_s H' U_s^{-1}$  into (10) which gives

$$G_s(t, t') = -i \frac{\text{Tr}\{T c_s(t) U(t) U^{-1}(t') c_s^+(t') e^{-\beta H'}\}}{\text{Tr}\{e^{-\beta H'}\}}; \quad (12)$$

where  $c_s(t)$  in the new representation is

$$c_s(t) = e^{iH't} c_s e^{-iH't} \quad (13)$$

and

$$U(t) = \exp\left[-\frac{\lambda}{\omega_0} (b^+(t) - b(t))\right]. \quad (14)$$

As  $G_s(t, t')$  is a function of  $t - t'$  it is sufficient to find  $G_s(t, 0)$ . For  $V_{sk}=0$  it is possible to calculate this Green's function exactly. In this case  $H'$  is diagonal so (13) and (14) become

$$c_s(t) = e^{-i(\varepsilon_s - v)t} c_s \quad (15)$$

$$U(t) = \exp\left[-\frac{\lambda}{\omega_0} (b^+ e^{i\omega_0 t} - b e^{-i\omega_0 t})\right]. \quad (16)$$

The Green's function can now be written\*

$$G_{so}(t, t') = \langle T c_s(t) c_s^+(t') \rangle \langle T U(t) U^{-1}(t') \rangle; \quad (17)$$

here  $\langle \rangle$  denotes thermal average.

The thermal average over the electron states is simple to carry out explicitly because, in the limit, only the adatom orbital contributes, and there are just the two possibilities of single and zero occupation of this state. The thermal average over the oscillator states is not quite so straightforward but can be performed by the use of a standard trick. The identity  $e^A e^B = e^{A+B} e^{1/2[A, B]}$ , applicable to operators  $A$  and  $B$  that have a c-number commutator, can be used to manipulate the plasmon operators into the form  $\exp\{i\alpha(\gamma b + \gamma^* b^+)\}$ . The thermal average of this operator is derived in Standard Texts in Quantum Mechanics<sup>11)</sup> and is  $\exp[-\frac{1}{2}\alpha^2 \gamma \gamma^* \coth \frac{1}{2}\beta \omega_0]$ . When this procedure is followed, and all the terms are collected, we have

$$G_{so}(t, 0) = -ie^{-i\varepsilon_s t} \exp\left\{-\frac{v}{\omega_0} (1 - \cos \omega_0 t)\right. \\ \times \coth[\beta \omega_0/2] \left.\right\} \left\{ \theta(t)(1 - n_s) \right. \\ \times \exp\left\langle ivt \left[ 1 - \frac{\sin \omega_0 t}{\omega_0 t} \right] \right\rangle \\ \left. - \theta(-t) n_s \exp\left\langle ivt \left[ 1 + \frac{\sin \omega_0 t}{\omega_0 t} \right] \right\rangle \right\} \quad (18)$$

where  $\theta(t)$  is the step-function and  $n_s = f(\beta(\varepsilon_s - v))$  is the Fermi function for the adatom orbital with a level shift due to image screening. Provided  $v/\omega_0 \ll 1$  the long time behaviour  $t \gg \omega_0^{-1}$  of this function approximates to the Green's function for a level at  $\varepsilon_s - v$ , because sufficient time has then elapsed for the plasmon cloud to adjust to the occupation of the adatom level. The characteristic time for the plasmon response is  $\omega_0^{-1}$ . For very short times  $t \ll \omega_0^{-1}$ , with  $n_s = 1$  the effective level is  $\varepsilon_s - 2v$  because the plasmon cloud has not had time to disperse after the removal of the electron. The effective level for  $t \ll \omega_0^{-1}$ ,  $n_s = 0$  is  $\varepsilon_s$  because of the plasmon delay in responding to the addition of the electron.

If the exponentials of the form  $\exp[v/\omega_0 \cdot f(t)]$  in (18) are expanded it is possible to Fourier

\*The subscript zero here implies that  $V_{sk}=0$ , whereas a superscript zero appears in the following to denote  $v=0$ .

transform (18) albeit in the form of an infinite series. The general expression is complicated but simplifies for  $\beta \rightarrow \infty$  to

$$G_{s0}(\omega) = \sum_{n=0}^{\infty} e^{-v/\omega_0} \frac{1}{n!} \left( \frac{v}{\omega_0} \right)^n \times \left[ \frac{1-n_s}{\omega - \varepsilon_s + v - n\omega_0 + i\delta} + \frac{n_s}{\omega - \varepsilon_s + v + n\omega_0 - i\delta} \right]; \quad \delta = 0^+. \quad (19)$$

Thus we get a series of poles with weights assigned according to a Poisson distribution. We can interpret the poles  $\omega = \varepsilon_s - v - n\omega_0$  that occur for  $n_s = 1$  as possible ionization energies for the adatom. For  $\omega_0/v \gg 1$  the peak of the Poisson distribution occurs at  $n=0$  so that the most likely value for the ionization energy is  $\omega = \varepsilon_s - v$ . However, for  $\omega_0/v \ll 1$  the maximum occurs when  $n \sim v/\omega_0$  plasmons are excited corresponding to an ionization energy  $\omega = \varepsilon_s - 2v$ , the ionization energy being distributed about this value with a width of order  $(\omega_0 v)^{1/2}$ . Similarly the poles that occur when  $n_s = 0$  correspond to the electron affinity, the most likely value being  $\varepsilon_s - v$  for  $\omega_0/v \gg 1$  and  $\varepsilon_s$  for  $\omega_0/v \ll 1$ .

#### §4. Perturbation Series in Powers of $v$

An alternative approach to calculating the one-electron Green's function  $G_s(t, t')$  at  $T_0 = 0$  is the employment of a standard Feynman Graph perturbation technique in powers of the interaction  $v$ . A rather similar technique has been used by Schrieffer and Mattis<sup>12)</sup> in treating the Anderson Hamiltonian, and we shall merely outline the formalism here. The Hamiltonian (6) is expressed in the form

$$H = H^0 + H_{int} \quad (20)$$

where

$$H^0 = \varepsilon_s n_s + \sum_k \varepsilon_k n_k + \sum_k [V_{sk} c_s^\dagger c_k + \text{H.c.}] + \omega_0 b^\dagger b \quad (21)$$

and

$$H_{int} = (v\omega_0)^{1/2} (b^\dagger + b) n_s. \quad (22)$$

Here eq. (9) has been used to eliminate  $\lambda$  from the Hamiltonian (6). The one-electron Green's function  $G_s(t, t')$  is expressed as a perturbation series in powers of  $H_{int}$ , in which each term corresponds to a Feynman diagram, the chief difference from the technique of Schrieffer and

Mattis being the suppression of spin and the replacement of Anderson's interaction  $U$  by the unperturbed ( $v=0$ ) boson Green's function

$$D^0(\omega) = \frac{2v\omega_0^2}{\omega^2 - \omega_0^2 + i\delta}; \quad \delta = 0^+. \quad (23)$$

(See for example Abrikosov, Gorkov, and Dzyalozhinskii ref. 13). We have here incorporated the coupling constant into the boson Green's function for convenience. The Fourier transform  $G_s^0(\omega)$  of the unperturbed Green's function  $G_s^0(t, t')$  replaces the  $G_d^0(\omega)$  of Schrieffer and Mattis:

$$G_s^0(\omega) = \left[ \omega - \varepsilon_s - \sum_k \frac{|V_{sk}|^2}{\omega - \varepsilon_k + i\delta \operatorname{sgn} \varepsilon_k} \right]^{-1}. \quad (24)$$

This may be conveniently written in Lehmann representation

$$G_s^0(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{A(\omega') d\omega'}{\omega - \omega' + i\delta \operatorname{sgn} \omega'}, \quad (25)$$

where

$$A(\omega) = \frac{\Delta(\omega)}{[\omega - \varepsilon_s - \Lambda(\omega)]^2 + \Delta^2(\omega)} \quad (26)$$

with

$$\Delta(\omega) = \pi \sum_k |V_{sk}|^2 \delta(\omega - \varepsilon_k),$$

$$\Lambda(\omega) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\Delta(\omega') d\omega'}{\omega - \omega'}. \quad (27)$$

Here  $P$  denotes the Cauchy principal value. We note that  $(1/\pi)A(\omega)$  is the unperturbed density of states projected into the adatom orbital. In the approximation where  $\Delta$  and  $\Lambda$  are treated as energy-independent constants, then  $A(\omega)$  becomes a Lorentzian function of width  $\Delta$  centred at  $\omega = \varepsilon_s + \Lambda$ .

Introducing the electron self-energy  $\Sigma_s(\omega)$  by

$$G_s(\omega) = \left[ \omega - \varepsilon_s - \Sigma_s(\omega) - \sum_k \frac{|V_{sk}|^2}{\omega - \varepsilon_k + i\delta \operatorname{sgn} \varepsilon_k} \right]^{-1}, \quad (28)$$

then the lowest order Feynman diagrams for  $\Sigma_s$  are as illustrated in Figs. 1a and 1b; a second order diagram is shown in Fig. 1d. We note that each broken line in a given diagram corresponds to the boson Green's function (23), and each full line to the electron Green's function (24), evaluation of the diagram otherwise proceeding in the standard way.<sup>13)</sup>

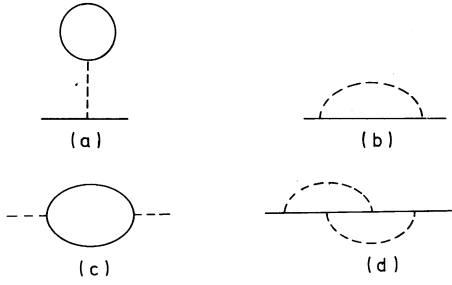


Fig. 1. (a, b, d): Contributions to electron self energy.  
(c): Zero order contribution to plasmon self energy.

(i) *Self energies to lowest order*

We begin by calculating  $\Sigma_s$  to first order in  $v$ , corresponding to the two diagrams of Figs. 1a and 1b. The diagram of Fig. 1a gives rise to the contribution

$$\Sigma_s^{(a)}(\omega) = -2v\langle n_s \rangle \quad (29)$$

where

$$\langle n_s \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} A(\omega) d\omega. \quad (30)$$

Here  $\langle n_s \rangle$  is the expectation value of the number of electrons in the adsorbed atom valence orbital.

Calculation of the diagram of Fig. 1b gives

$$\Sigma_s^{(b)}(\omega) = \frac{v\omega_0}{\pi} \int_{-\infty}^{\infty} \frac{A(\omega') d\omega'}{\omega - \omega' + (i\delta - \omega_0) \operatorname{sgn} \omega'}. \quad (31)$$

The first order self energy is the sum of these contributions

$$\Sigma_s(\omega) = \Sigma_s^{(a)}(\omega) + \Sigma_s^{(b)}(\omega). \quad (32)$$

Note that the imaginary part of  $\Sigma_s^{(b)}$  may be obtained to within a constant of proportionality by cutting  $A(\omega) \operatorname{sgn} \omega$  at  $\omega=0$  and displacing the two halves for  $\omega \geq 0$  to  $\omega = \pm \omega_0$  respectively. Whereas  $\Sigma_s^{(a)}$  is entirely real,  $\operatorname{Im}\Sigma_s^{(b)}(\omega)$  is nonzero if  $|\omega| > \omega_0$ .

If  $\omega_0$  is small,  $\Sigma_s$  may be calculated up to first order in  $\omega_0$  by putting  $\omega_0=0$  in the integral of (31), when we have

$$\Sigma_s(\omega) = -2v\langle n_s \rangle + v\omega_0 G_s^0(\omega) + O(\omega_0^2). \quad (33)$$

Near  $\omega = \varepsilon_s$ , the pole in the unperturbed  $G_s^0(\omega)$ , the second term in (33) is just  $v\omega_0 G_s^0(\varepsilon_s)$ , which is of order  $v\omega_0/\pi\Delta$ . Provided  $\omega_0 \ll \Delta$  this term may be neglected, and putting  $\varepsilon_{\text{eff}} \equiv \varepsilon_s + \Sigma_s$ , we have

$$\varepsilon_{\text{eff}} = \varepsilon_s - 2v\langle n_s \rangle; \quad \omega_0 \ll \Delta. \quad (34)$$

In this limit only the diagram of Fig. 1a contributes.

In the opposite limit of large  $\omega_0$  at a given frequency  $\omega$  then  $\operatorname{Im}\Sigma_s^{(b)}(\omega)$  is zero and  $\operatorname{Re}\Sigma_s^{(b)}(\omega)$  can be expanded in descending powers of  $\omega_0$ :

$$\operatorname{Re}\Sigma_s^{(b)}(\omega) = v(2\langle n_s \rangle - 1) - \frac{v}{\omega_0}(\omega - \bar{\varepsilon}_s) + O(\omega_0^{-2}). \quad (35)$$

We have used (30) together with the definition

$$\bar{\varepsilon}_s = \frac{1}{\pi} \int_{-\infty}^{\infty} \omega' A(\omega') d\omega' \quad (36)$$

and the sum rule

$$\frac{1}{\pi} \int_{-\infty}^{\infty} A(\omega') d\omega' = 1. \quad (37)$$

When looking for the pole in  $G_s(\omega)$ ,  $\omega$  in (35) is to be interpreted as  $|\omega - \varepsilon_s| \leq \Delta$ , so that if  $\omega_0 \gg \Delta$  the second term in (35) may be neglected. Then using (29) and (32) we have to first order in  $v$ :

$$\varepsilon_{\text{eff}} = \varepsilon_s - v; \quad \omega \gg \Delta. \quad (38)$$

Recalling the definition (1) of  $\varepsilon_s$ , we see that (34) is identical with the approximation (2) discussed in the Introduction, whereas (38) is identical with (3). In (34) the period of the plasmon oscillator has been assumed long compared with  $\Delta^{-1}$  i.e. the electron lifetime in the adatom orbital, consistent with the idea of a static image discussed in the Introduction. The converse assumption on which (38) is based, that  $\omega_0$  is large compared with  $\Delta$ , is physically consistent with the concept of an image able to follow the fluctuating adatom charge adiabatically. Hence the terms static and adiabatic approximations are loosely used to describe the respective approximations.

A boson self-energy  $\Pi(\omega)$  may be introduced corresponding to a renormalization of the Green's function (23) to  $D(\omega) = [D^0(\omega)^{-1} - \Pi(\omega)]^{-1}$ . The lowest order approximation to  $\Pi(\omega)$  is the second order diagram of Fig. 1c. When  $\omega_0 \ll \Delta$  the effect of  $\Pi(\omega)$  is to shift the surface plasmon pole in  $D(\omega)$  to the renormalised frequency

$$\omega'_0 = \omega_0(1 + v\Pi^0(0)). \quad (39)$$

In fact  $\Pi^0(0) < 0$  and of order  $\Delta^{-1}$ , implying a reduction in the frequency of the slowly moving

oscillator by the static "polarizability" of the adsorbate. In contrast to this, there is no significant correction to  $\omega_0$  when  $\omega_0 \gg \Delta$ .

In addition to shifts in  $\omega_0$ , which may be readily separated when  $\omega_0$  is very different from  $\Delta$ , there is structure in  $D(\omega)$  when  $\omega \sim \Delta$  due to the electron-hole excitations present in  $\Pi(\omega)$ . This effect is similar to that of electron-hole excitations in the substrate which were neglected in formulating our Hamiltonian and we shall not discuss this rather complicated problem further here.

(ii) *Adiabatic approximation to  $\Sigma_s$  beyond first order*

The first order approximation of §4 (i) implied sufficiently small  $v$  compared with  $\Delta$  and  $\varepsilon_s$ . Now for the calculation of higher order diagrams a simplification which suggests itself is the replacement of  $D^0(\omega)$  by its adiabatic limit

$$D^0(\omega) = -2v, \quad \omega_0 \gg \omega. \quad (40)$$

If however this limit were taken prior to evaluation of the diagram of Fig. 1b, this integral would no longer converge at large values of the argument of the electron Green's function, and taking the limit (40) before evaluation of the diagram is incorrect, a problem which disappears in higher order. It would appear that this difficulty can be removed by working with  $G_s^1(\omega)$ , which differs from  $G_s^0(\omega)$  in that  $\varepsilon_s$  is replaced by  $\varepsilon_{\text{eff}}$  in the adiabatic limit (38), provided that we now exclude all self energy corrections of the type Fig. 1a and 1b from the diagram technique.

Taking the limit (40) now being permissible, our diagrams correspond to the trivial perturbation  $H_{\text{int}} = -2vn_s n_s$  and should cancel. Thus in second order there are only two diagrams, Fig. 1d together with a diagram obtained by inserting the boson self-energy part Fig. 1c into the boson line of Fig. 1b; these diagrams are identical but of opposite sign within our approximation. A similar cancellation is demonstrable in 3rd order. Assuming the cancellation occurs in all orders, then the corrections to the adiabatic approximation (38) apparently vanish when  $\omega_0$  sufficiently large.

The above result should be interpreted with caution, since in the exact result (19) for  $V_{sk} = 0$  the strength of the adiabatic peak in the spectral density of  $G_s(\omega)$ , which goes as

$\exp(-v/\omega_0)$ , becomes very small if  $v \gg \omega_0$ . An alternative approach to the problem is considered in §5.

(iii) *Static approximation to  $\Sigma_s$  beyond first order*

When  $\omega_0 \rightarrow 0$  but  $v$  not small it may be argued that only diagrams with all boson lines terminating in a closed loop (*i.e.* transmitting zero frequency) contribute significantly to  $\Sigma_s$ . This is equivalent to retaining only Fig. 1a in a self-consistent approximation. The equations for this approximation, very similar to those of the original Anderson impurity model<sup>9)</sup> are therefore, from (34) and (28), given by

$$\Sigma_s = -2v \langle n_s \rangle \quad (41a)$$

where

$$\langle n_s \rangle = \frac{1}{2\pi i} \times \int_C \left[ \omega - \varepsilon_s - \Sigma_s - \sum_k \frac{|V_{sk}|^2}{\omega - \varepsilon_k + i\delta \operatorname{sgn} \varepsilon_k} \right]^{-1} d\omega. \quad (41b)$$

( $C$  is an anti-clockwise contour consisting of the real axis together with an infinite semicircle in the upper half plane).

The graphical solution of (41) is sketched in Fig. 2 for two values of  $v$  in the case of a Lorentzian level distribution  $A(\omega)$ , taking  $\varepsilon_s > 0$ . The straight lines represent eq. (41a) and the curve eq. (41b). For the smaller value of  $v$  (full line) the single intersection with the curve represents a normal self-consistent Hartree solution of the problem. This method seems to be in principle the same as used by some earlier authors, *e.g.* Bennett and Falicov<sup>2)</sup> although our Hamiltonian is especially simple.

For the larger value of  $v$  (broken line) illustrated in Fig. 2,  $v$  here being comparable with

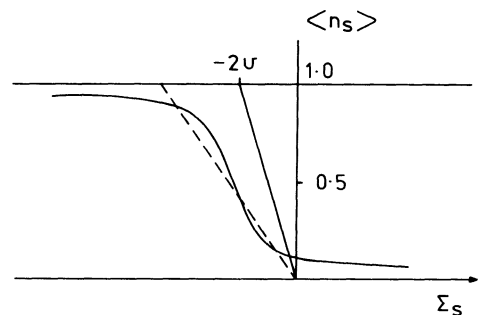


Fig. 2. Self-consistency plot in static approximation (see text).

$\Delta$ , a triple intersection occurs presumably corresponding to an instability of the normal solution represented by the central intersection. It does not seem, however, that the conditions  $\omega_0 \ll \Delta \sim v$  are likely to be of common occurrence, and we have not investigated this possibility further here.

### §5. Perturbation Series in Powers of $V_{sk}$

Instead of a perturbation theory in powers of the interaction  $v$  we can develop a theory in powers of the overlap  $V_{sk}$ . This approach helps to resolve some of the problems that arose in §4 (ii) in considering the adiabatic limit. The electron-plasmon interaction term in  $H$  is retained in the unperturbed part of the Hamiltonian  $H_0$ . This complicates matters because the Wick's decomposition of the perturbation terms into one-particle propagators cannot be carried out when two-body interaction terms are retained in  $H_0$ , so the Feynman diagram technique is not applicable. However, Hubbard<sup>14)</sup> has developed a perturbation theory of narrow energy bands, using an unperturbed Hamiltonian that includes the atomic interactions and an expansion in powers of the kinetic energy or hopping, that can be taken over for our purposes with minor modifications.

The diagrams in this theory have *vertices* labelled according to the *states* of  $H_0$ , and *lines* that represent a transfer of an electron from one state to another at a particular time. The internal lines contribute a factor  $iV_{sk}$  and correspond to an imaginary time  $\tau$  such that  $0 < \tau < i\beta$ . Second order contributions in  $V_{sk}$  to  $G_s(\tau, \tau')$  are shown in Fig. 3.

A full prescription for drawing diagrams and writing down contributions is given in Hubbard's paper. For our case we note that any number of pairs of lines can enter and leave an  $s$ -vertex (which may be repeated), and each of these vertices contributes a factor equal to the cumulant Green's function corresponding to the time labels of the lines running into and out of the vertex. For instance, the  $s$ -vertex in Fig. 3a contributes

$$\langle Tc_s(\tau)c_s^+(\tau_1)c_s(\tau_2)c_s^+(\tau') \rangle_c \quad (42)$$

where  $\langle \rangle$  indicates a thermal average with respect to  $H_0$ . The subscript  $c$  denotes the cumulant function, which can always be expressed in terms of the corresponding many-

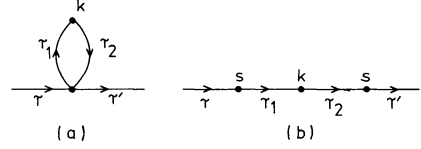


Fig. 3. Contributions to  $G_s(\omega)$  in Hubbard perturbation technique.

time Green's functions of the same and lower orders. For example, in this case,

$$\begin{aligned} & \langle Tc_s(\tau)c_s^+(\tau_1)c_s(\tau_2)c_s^+(\tau') \rangle_c \\ &= \langle Tc_s(\tau)c_s^+(\tau_1)c_s(\tau_2)c_s^+(\tau') \rangle \\ & - \langle Tc_s(\tau)c_s^+(\tau_1) \rangle \langle Tc_s(\tau_2)c_s^+(\tau') \rangle \\ & - \langle Tc_s(\tau)c_s^+(\tau') \rangle \langle Tc_s^+(\tau_1)c_s(\tau_2) \rangle. \end{aligned} \quad (43)$$

These Green's functions can be evaluated by the procedure used to calculate  $G_{s0}(t, t')$  as described earlier. Unlinked diagrams cancel in the final sum and need not be taken into account.

When  $H_0$  is a one-body Hamiltonian Wick's Theorem is applicable and the many-time Green's function can be reduced to products of double time Green's functions; the net result is that cumulant Green's functions with more than two time labels vanish. For this reason the  $k$ -vertices have only one line entering and one line leaving. Hence, a  $k$ -vertex, as in Fig. 3a, contributes

$$\langle Tc_k(\tau_1)c_k^+(\tau_2) \rangle. \quad (44)$$

Finally each diagram carries a symmetry and sign factor. A sum is taken over the  $k$ -sites and the internal times are integrated over the interval  $(0, i\beta)$ .

In the extreme adiabatic limit  $\omega_0 \rightarrow \infty$ ,  $s$ -vertices that have more than two lines associated with them give zero contribution, and the only relevant diagrams are in the form of the linked chains shown in Fig. 4. The details of the argument are in the appendix. There is no difficulty in carrying out the summation of the chain diagrams to all orders, and the result for the Fourier transform of  $G_s(t, t')$  (where we have made an analytic continuation to real times) is

$$G_s(\omega) = \left[ \omega - \varepsilon_s + v - \sum_k \frac{|V_{sk}|^2}{\omega - \varepsilon_k} \right]^{-1}. \quad (45)$$

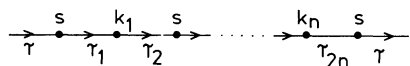


Fig. 4. Chain graph contribution to  $G_s(\omega)$ .



This confirms the conjecture in §4 (ii) that the self-energy  $\Sigma_s$  is given entirely by the first order term (in powers of  $v$ ) in this limit. We might have anticipated this result because if the limit  $\omega_0 \rightarrow \infty$  is taken in the transformed Hamiltonian  $H'$  the boson factor that modifies the electron hopping term tends to unity and the Hamiltonian effectively becomes a one-body one.

An approximate expression for  $G_s(\omega)$  can be obtained by summing the chain diagrams for finite  $\omega_0$ . The result is

$$G_s(\omega) = \left[ G_{s0}(\omega)^{-1} - \sum_k \frac{|V_{sk}|^2}{\omega - \varepsilon_k} \right]^{-1}, \quad (46)$$

where  $G_{s0}$  refers to (19). This result is exact when  $\omega_0 \rightarrow \infty$  as discussed above, and also in the limit  $v \rightarrow 0$ . It also seems to link up, at least qualitatively, with the static approximation discussed in §4 (i) and (iii). For  $\omega_0 \ll \Delta < v$  the peaks in the adsorbed atom density of states derived from (46) occur at  $\omega \sim \varepsilon_s - 2v$  and  $\varepsilon_s$  corresponding to the solutions indicated in Fig. 2, by the intersections of the dotted line at  $n_s \sim 1$  and  $n_s \sim 0$ . In the regime  $\omega_0 < v < \Delta$ , the broadening due to the mixing of the adatom states with those of the metal is such that these peaks merge giving a single peak somewhere in the region of the stable Hartree Fock solution corresponding to the intersection with the full line in Fig. 2.

## §6. Conclusion

A simple model Hamiltonian has been used to discuss the effect of the image force on the chemisorption of an atom possessing a single nondegenerate valence orbital  $|s\rangle$ , electron spin being ignored. The effect of the image force on the electron is expressed as an electron-surface plasmon interaction. The model has been formulated with special reference to the case of alkali atoms adsorbed on transition metals at low coverage. We have emphasised the calculation of the one-electron Green's function for the adatom orbital, which contains the local density of states projected into the adatom orbital from which the mean number of electrons  $\langle n_s \rangle$  on the adatom may be determined by integration over energy. Under some conditions the effect of the image force may be expressed simply as an upwards shift in the adatom valence level from its free atom value

$\phi - I$  to an effective value  $\varepsilon_{\text{eff}}$ ; knowledge of  $\varepsilon_{\text{eff}}$  is important in calculations of work function variations in alkali adsorption on transition metals.<sup>10)</sup> It is also hoped that the application of current techniques sensitive to the adatom density of states may yield direct experimental information on the latter quantity.

The basic parameters in the present model are the surface plasmon frequency  $\omega_0$ , the coupling strength  $v = e^2/4d$  and, in cases where the local adatom density of states in the absence of the image force is a well defined Lorentzian, the width  $\Delta$  of the latter. If  $\Delta \gg v$ , the straightforward first order self energy calculation of §4 should be valid. In that section it was shown that if  $\omega_0 \ll \Delta$  then  $\varepsilon_{\text{eff}} = \phi - I + 2v(1 - \langle n_s \rangle)$  (Static Approximation) and if  $\omega_0 \gg \Delta$  then  $\varepsilon_{\text{eff}} = \phi - I + v$  (Adiabatic Approximation). The static and adiabatic approximations imply respectively that the surface plasmon period be much longer or much shorter than the lifetime of an electron in the adatom valence orbital. An extension of the region of validity of the adiabatic result into the intermediate coupling regime was implied by the discussion of §4 (ii), in accordance with the derivation of the adiabatic result without the assumption that  $\Delta$  be large given in §5. An extension of the static result into the regime  $\Delta \gtrsim v$ , provided  $\omega_0$  sufficiently small, was also shown to be possible in §4 (iii), provided  $\langle n_s \rangle$  appearing in (34) was determined self-consistently. The formulation in this limit is the same as a self-consistent Hartree calculation.

In a case such as Caesium adsorbed on tungsten or rhenium,  $\Delta$  has been estimated<sup>10)</sup> to be of order 1 eV and  $v$  to be about 2 eV. The surface plasmon frequency of molybdenum is believed to be about 10 eV,<sup>15)</sup> and a similar result is probably true for tungsten. Thus the condition  $\Delta \sim v \ll \omega_0$  for the adiabatic approximation is reasonably well satisfied so we would expect that  $\varepsilon_{\text{eff}} = \phi - I + v$ . Since the caesium is largely ionised at low coverage ( $\langle n_s \rangle$  small<sup>2,3,10)</sup>) the static approximation will yield an energy shift due to the image effect almost twice as large. The value of  $\varepsilon_{\text{eff}}$  estimated from experimental work function changes in ref. 10 is actually somewhat lower even than the adiabatic result. The conditions for the validity of the adiabatic result may not however be so well satisfied in the case of sub-

strates such as nickel or copper having considerably lower plasma frequencies. First principles theoretical studies of alkali-transition metal adsorption in the literature in some cases employ the adiabatic approximation,<sup>3)</sup> and in others the static approximation.<sup>2)</sup>

It is worth contrasting the above conclusions with a case such as  $v \gg \omega_0 \gg \Delta$ , although we do not normally find  $v \gg \omega_0$  when  $\omega_0$  is a surface plasma frequency. The adatom Green's function given in eq. (19) for  $\Delta=0$  shows two peaks in the density of states of width  $\sim \sqrt{\omega_0 v}$  at  $\omega = \phi - I$  and  $\omega = \phi - I + 2v$ . In the interesting case  $-2v < \phi - I < 0$  the positions of the peaks are given by selecting the outer pair of the triple roots occurring in the static approximation (see Fig. 2), but the peak widths, arising from many-plasmon excitations, do not appear in this approximation. When  $\Delta$  is finite but  $v \gg \omega_0 \gg \Delta$  the width  $\Delta$  when  $v=0$  (no image force) is small compared with the many-boson width  $\sqrt{v\omega_0}$  and the Green's function is unlikely to resemble that when  $v=0$  at all closely.

The existence of electron spin has in this paper been ignored for simplicity. An important effect brought in with the inclusion of spin degeneracy is the Coulomb interaction  $U$  between two electrons of opposite spin in the adatom orbital  $|s\rangle$ .<sup>9)</sup> In the Introduction it was shown that if the electron can be assumed to be always followed by its image then the ionization energy  $I'$  of the adatom is given by the adiabatic result  $I' = I - v$ . Extension of the assumption to a pair of electrons on the adatom yields an electron affinity  $A' = I - U + v$ . The effective value of  $U$  is thus  $U_{\text{eff}} = I' - A' = U - 2v$ .  $U$  can thus be very considerably reduced by screening, as emphasised by Schrieffer<sup>16)</sup> and assumed by Muscat and Newns.<sup>10)</sup> The derivation breaks down unless the image is assumed to follow each electron, and the screening is thus probably confined to the adiabatic regime, assuming our results are not greatly perturbed by spin degeneracy and the presence of  $U$ .

The representation of the image force in terms of electron-surface plasmon interaction is not exact even at large  $d$ , owing to the existence of low energy electron-hole excitations, as pointed out by Harris and Jones.<sup>17)</sup> As pointed out in §4 (i), electron-hole excitations also appear in the boson propagator even though neglected in the original Hamiltonian. Though

their effect could well be appreciable, the inclusion of these excitations would not necessarily vitiate our discussion of the surface plasmon degree of freedom. Treatment of the electron-hole excitations may encounter an infra-red divergence problem.<sup>18)</sup>

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### Appendix

To calculate the many-time Green's functions, such as

$$\langle T c_s(\tau_1) c_s(\tau_2) c_s^+(\tau'_1) c_s^+(\tau'_2) \rangle \quad (\text{A1})$$

with respect to  $H_0$  we generalize the procedure given for the calculation of  $G_{s_0}(t, t')$ . Contributions occur only for the time orderings in which the creation and annihilation operators alternate. A typical term in (A1) is

$$-\theta(\tau - \tau'_1) \theta(\tau_2 - \tau'_2) \theta(\tau'_1 - \tau_2) \times \langle c(\tau_1) c^+(\tau'_1) c(\tau_2) c^+(\tau'_2) \rangle. \quad (\text{A2})$$

To evaluate this term we use the diagonal form of  $H'_0 = UH_0U^{-1}$  so it becomes

$$-\theta(\tau_1 - \tau'_1) \theta(\tau_2 - \tau'_2) \theta(\tau'_1 - \tau_2) \times \exp[-(\epsilon_s - v)(\tau_1 + \tau_2 - \tau'_1 - \tau'_2)] \times n_s \langle U(\tau_1) U^{-1}(\tau'_1) U(\tau_2) U^{-1}(\tau'_2) \rangle_B \quad (\text{A3})$$

on evaluating over the electron states, where  $\langle \rangle_B$  indicates a thermal average with respect to the boson states. The plasmon operators are manipulated into the form  $\exp\{i\alpha(\gamma b + \gamma^* b^+)\}$  by using the operator identity, given in the paragraph proceeding equation (18), twice. On taking the expectation value of this we find

$$\langle U(\tau_1) U^{-1}(\tau'_1) U(\tau_2) U^{-1}(\tau'_2) \rangle_B = \frac{F(\tau_1 - \tau'_1) F(\tau_2 - \tau'_2) F(\tau_1 - \tau'_2) F(\tau'_1 - \tau_2)}{F(\tau'_1 - \tau'_2) F(\tau_1 - \tau_2)} \quad (\text{A4})$$

where

$$\log_e F(\tau) = -\frac{v}{2\omega_0} \left\{ \coth \frac{\beta\omega_0}{2} - e^{-i\omega_0\tau} \left( \coth \frac{\beta\omega_0}{2} + 1 \right) + e^{i\omega_0\tau} \left( 1 - \coth \frac{\beta\omega_0}{2} \right) \right\}. \quad (\text{A5})$$

The other contributions to (A1) can be calculated in a similar way. The method can be used for Green's functions involving any number of times and the pattern that emerges in (A4) can be generalized. In the limit  $\omega_0 \rightarrow \infty$ ,  $F(\tau) \rightarrow 1$  and all Green's functions are the same as those for a one-body Hamiltonian  $H_0 = (\epsilon_s - v)n_s$ . These many-time Green's functions can be reduced to products of double time Green's functions applying Wick's Theorem and so the corresponding cumulant Green's functions involving more than two time arguments vanish.

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