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Screening in chemisorption theory

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A theory is presented that makes it possible to discuss the effect of plasmon screening on the chemisorption energy as a function of the bond strength/plasmon energy ratio. The correlation effects are shown to disappear for strong bonding and to cancel out in the limiting case of weak bonding. Significant effects are found in the intermediate bonding range, when the tunneling frequency of the adsorbate electrons is of the same order of magnitude as the plasmon frequency. For values representative of chemisorption of hydrogen to a transition-metal surface the contribution to the bond energy may be of the order of 20%. The quantum theoretical analysis leads to effective potentials, which can be readily incorporated into the Newns-Anderson-type chemisorption Hamiltonian. Explicit expressions for the screened exchange and the Coulomb hole contributions are derived.

I. INTRODUCTION

The notion that chemisorption can be considered localized now appears well established.^{1,2} It implies that Coulomb interactions have to be screened.

When chemisorption is weak, the metallic nature of the substrate will determine the nature of the screening interactions. Once the chemisorptive bond has become covalent, the situation becomes less clear and at least part of the localization arises from the formation of a "surface molecule" embedded in a metallic matrix.³

Hewson and Newns⁴ demonstrated for the image potential using a model Hamiltonian containing a plasmon interaction term, that dynamic screening effects become increasingly important with increasing strength of the chemisorptive bond.

Kranz and Griffin⁵ extended their work by developing a general theory for chemisorption incorporating screening effects. They conclude that in the limiting case of weak chemisorption, significant effects in the adsorbate electron density appear, but that there is no effect on the chemisorption energy.

It is our aim to extend the theory in order to be able to study the effect of screening for weak as well as strong bonding. This is important since chemisorption usually occurs in the intermediate region. A calculation of the contribution of the image potential to the chemisorption energy requires consideration of changed electrostatic interactions at the metal surface. The range of the electrostatic interactions contributing to the Hartree term is finite, since the long-range interaction with the electrons is compensated for by the interaction with the nuclei. This compensation is absent for the exchange term. The range of the exchange interactions is determined by static screening for weak chemisorption, modified by dynamic screening terms when the interaction increases. So an approach is required that incorporates electron correlation.

In the limiting case of strong chemisorption the screening length of the exchange terms becomes of the range of the decay length of the chemisorption induced surface states.

Kadanoff and Baym⁶ have developed equations for the exchange-correlation potential, which can be readily con-

verted to expressions showing the intimate relation between static and dynamic screening.⁷ These equations are used to derive an expression for the effective exchange-correlation potential valid in the random phase approximation that can be used over the full range of the chemisorption bond strength for a hydrogen-type adsorbate. The correlation part of this potential is considered as a perturbation and Dyson's equations⁸ are used to derive the chemisorption Hamiltonian. Explicit expressions for the self-energy term are derived. Finally, the results are incorporated in a Newns-Anderson⁹-type Hamiltonian and the effect on the chemisorption bond strength is studied as a function of the adsorbate-metal interaction.

II. DERIVATION OF FUNDAMENTAL EQUATIONS

The exact integro-differential equation for the single particle Green's function in a time-independent external field $V_0(\mathbf{r})$ is⁶

$$\left\{ i \frac{\partial}{\partial t} + \nabla^2 - U_{\text{eff}}(\mathbf{r}) \right\} G(t-t'; \mathbf{r}-\mathbf{r}') + \int_0^\infty dt \int d\mathbf{r} \sum (t-t; \mathbf{r}-\mathbf{r}) G(t-t'; \mathbf{r}-\mathbf{r}') = -\delta(t-t') \cdot \delta(\mathbf{r}-\mathbf{r}'). \quad (2.1)$$

The Hartree potential U_{eff} is defined as

$$U_{\text{eff}}(\mathbf{r}) = V_0(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}') - \sum_I Z_I \delta(\mathbf{r}-\mathbf{r}_I) \quad (2.2)$$

with $n(\mathbf{r})$ the electron density and Z_I the charge of the nuclei.

The self-energy function Σ is the solution of the equation:

$$\begin{aligned} & \sum (t-t; \mathbf{r}-\mathbf{r}) \\ &= iV_s(t-t; \mathbf{r}-\mathbf{r})G(t-t; \mathbf{r}-\mathbf{r}) \\ &+ \int dt' \int d\mathbf{r}' \int dt'' \int d\mathbf{r}'' V_s(t-t'; \mathbf{r}-\mathbf{r}') \\ &\quad \times G(t-t''; \mathbf{r}-\mathbf{r}'') \frac{\partial \sum(t''-t; \mathbf{r}''-\mathbf{r})}{\delta U_{\text{eff}}(t'; \mathbf{r}')}. \end{aligned} \quad (2.3)$$

The screened Coulomb potential V_s is a solution of the equation:

$$\begin{aligned}
 V_s(\mathbf{t} - \mathbf{t}'; \mathbf{r} - \mathbf{r}') &= V(\mathbf{r} - \mathbf{r}') + i \int d\mathbf{t}'' \int d\mathbf{r}'' \int d\mathbf{t}''' \int d\mathbf{r}''' \\
 &\cdot V_s(\mathbf{t} - \mathbf{t}''; \mathbf{r} - \mathbf{r}'') G(\mathbf{t}'' - \mathbf{t}'''; \mathbf{r}'' - \mathbf{r}''') \\
 &\times G(\mathbf{t}'' - \mathbf{t}''''; \mathbf{r}'' - \mathbf{r}''''') V(\mathbf{r}'''' - \mathbf{r}') \\
 &- i \int d\mathbf{t}'' \int d\mathbf{r}'' \int d\mathbf{t}''' \int d\mathbf{t}'''' \int d\mathbf{r}'''' \int d\mathbf{t}'''''' \int d\mathbf{r}'''''' \\
 &\cdot V_s(\mathbf{t} - \mathbf{t}''; \mathbf{r} - \mathbf{r}'') G(\mathbf{t}'' - \mathbf{t}'''; \mathbf{r}'' - \mathbf{r}''') \\
 &\times \frac{\partial \Sigma(\mathbf{t}'', \mathbf{r}'', \mathbf{t}''', \mathbf{r}''')}{\partial U_{\text{eff}}(\mathbf{t}'', \mathbf{r}'')} \\
 &\times G(\mathbf{t}'' - \mathbf{t}''''; \mathbf{r}'' - \mathbf{r}''''') V(\mathbf{r}'''' - \mathbf{r}'). \quad (2.4)
 \end{aligned}$$

These equations can be transformed to time independent matrix equations in a discrete basis set using the definitions

$$G(\mathbf{t} - \mathbf{t}'; \mathbf{r} - \mathbf{r}') = \int dE \sum_{i,j} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}') e^{iE(\mathbf{t} - \mathbf{t}')} G_{ij}(E), \quad (2.5)$$

$$H_{ij}^0 = \int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \{ -\nabla_{\mathbf{r}}^2 + U_{\text{eff}}(\mathbf{r}) \}, \quad (2.6)$$

$$V(ij|kl) = \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.7)$$

with

$$\sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (2.8)$$

$$\int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) = \delta_{ij}. \quad (2.9)$$

As a result Eqs. (2.1) and (2.4) are converted to

$$EG_{im}(E) - \sum_k \left[H_{ik}^0 + \sum_{ik}(E) \right] G_{km}(E) = \delta_{im} \quad (2.10)$$

with the self-energy term

$$\begin{aligned}
 \sum_{ik}(E) &= i \sum_{j,s} \int dE' V^s(ij|pq; E - E') G_{js}(E') \\
 &\cdot \{ \delta_{qk} \delta_{ps} + S(s, p; E' | q, k; E) \} \quad (2.11)
 \end{aligned}$$

with

$$\begin{aligned}
 S(s, p; E' | q, k; E) &= \int d(\mathbf{t}'' - \mathbf{t}') \int d(\mathbf{t}' - \mathbf{t}) e^{iE'(\mathbf{t}'' - \mathbf{t}')} \\
 &\times e^{iE(\mathbf{t}' - \mathbf{t})} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r} \\
 &\times \phi_s^*(\mathbf{r}'') \phi_p(\mathbf{r}') \phi_q^*(\mathbf{r}') \phi_k(\mathbf{r}) \frac{\partial \Sigma(\mathbf{t}'' - \mathbf{t}; \mathbf{r}'' - \mathbf{r})}{U_{\text{eff}}(\mathbf{t}', \mathbf{r}')}. \quad (2.12)
 \end{aligned}$$

The equation for the screened potential becomes

$$\begin{aligned}
 V^s(ij|kl; E) &= V(ij|kl) - \sum_{\substack{r,s \\ p,q}} V^s(ij|rs; E) \\
 &\cdot V(pq|kl) \cdot \mu(pr, sq; E) \quad (2.13)
 \end{aligned}$$

with

$$\begin{aligned}
 \mu(pr|sq; E) &= i \int dE' \sum_{l,k} G_{pl}(E + E') G_{kq}(E') \\
 &\cdot \{ \delta_{lr} \delta_{ks} + S(l, r, E + E'; k, q, E') \}, \quad (2.14)
 \end{aligned}$$

the self-energy term Σ reduces to the exchange energy contribution if screening effects are neglected.

Fourier transformation of Eq. (2.4) enables one to solve the Fourier transform of V^s :

$$V^s(E, \mathbf{q}) = \frac{1}{1 + [\lambda^2(E, \mathbf{q})/q^2]} \cdot \frac{e^2}{q^2} = \frac{1}{\epsilon(E, \mathbf{q})} \frac{e^2}{q^2} \quad (2.15)$$

with

$$\begin{aligned}
 \lambda^2(E, \mathbf{q}) &= i \int dE' \int d\mathbf{q}' G(E + E', \mathbf{q} + \mathbf{q}') \cdot G(E, \mathbf{q}') \\
 &\cdot \{ 1 + S(E + E', \mathbf{q} + \mathbf{q}'; E', \mathbf{q}') \}. \quad (2.16)
 \end{aligned}$$

In the adiabatic limit one finds that static screening length λ_s^{-1} becomes

$$\lambda_s = \lim_{E \rightarrow 0} \lim_{q \rightarrow 0} \lambda(E, \mathbf{q}). \quad (2.17)$$

Incorporating effects due to S leads to corrections beyond the random phase approximation. So in the following we will ignore S .

The dielectric function $\epsilon(E, \mathbf{q})$ has been extensively studied in the random phase approximation. We will incorporate dynamic effects by using Inkson's¹⁰ model dielectric function, which has been shown to be of general use¹¹:

$$\begin{aligned}
 \frac{1}{\epsilon(E, \mathbf{q})} &= 1/1 + \frac{\lambda_s^2}{q^2} \left\{ 1 - \frac{\frac{\lambda_s^2}{q^2} \left(\frac{1}{\epsilon_0 - 1} - \frac{E^2}{\omega_p^2} \right)}{1 + \frac{\lambda_s^2}{q^2} \left(\frac{1}{\epsilon_0 - 1} - \frac{E^2}{\omega_p^2} \right)} \right\} \quad (2.18)
 \end{aligned}$$

with $\hbar = 1$. ϵ_0 is the dielectric function of the metal, and ω_p the plasmon frequency. We will use Eq. (2.18) with $\epsilon_0 \rightarrow \infty$, as is the case for a metal.

We will use the matrix equations (2.10) for the single-particle Green function G_{im} in the random phase approximation.

In Hartree-Fock theory the self-energy term Σ_{ik} reduces to

$$\sum_{ik}^{\text{HF}, \sigma} = i \sum_{jp} \int dE' V(ij|pk) G_{jp}^{\sigma}(E'), \quad (3.1)$$

where σ labels the spin of the electron. Expression (3.1) represents the Hartree-Fock exchange energy term. We will incorporate this contribution into the Hartree-Fock unperturbed Hamiltonian.

The correlation energy term Σ^c will be considered a perturbation:

$$\sum_{ik}^{c,\sigma}(E) = \sum_{ik}^{\sigma}(E) - \sum_{ik}^{\text{HF},\sigma} \quad (3.2)$$

Expression (3.2) involves the approximation that the Green functions do not couple different spin states.

Using the resolvent method⁸ one finds to lowest order:

$$G_{ii} = \frac{1}{G_{ii}^{0-1} - G_{ii}^{0-1} \sum_j G_{ij}^0 \sum_{j'}^c} \quad (3.3)$$

with G_{ii}^0 the Green function solution corresponding to the Hartree-Fock solution.

We will evaluate expressions (2.10) and (2.11) using the zero differential overlap approximation for the matrix elements V and V^s :

$$V(ij|kl) = \delta_{ij} \delta_{kl} V_{ik}, \quad (3.4)$$

$$V^s(ij|kl, E) = \delta_{ij} \delta_{kl} V_{ik}^s(E).$$

Equation (2.13) then reduces to the form:

$$V_{ii}^s(E) = V_{ii} - \sum_{j,k} V_{ij}^s(E) \cdot V_{ki} \cdot \mu(kj|jk, E). \quad (3.5)$$

We will divide this equation into terms defined on the adsorbate ($i = 0$) and on the metal

$$\begin{aligned} V_{00}^s(E) &= V_{00} - V_{00}^s(E) \cdot V_{00} \cdot \mu(00|00, E) \\ &\quad - \sum_{j \neq 0} V_{0j}^s(E) \cdot \mu(j0|j0, E) V_{00} \\ &\quad - \sum_{\substack{j \neq 0 \\ k \neq 0}} V_{0j}^s(E) \cdot \mu(jk|kj, E) V_{0k}, \end{aligned} \quad (3.6a)$$

$$\begin{aligned} V_{01}^s(E) &= V_{01} - V_{00}^s(E) \cdot \sum_j \mu(0j|j0, E) \cdot V_{j1} \\ &\quad - \sum_{k \neq 0} V_{0k}^s(E) \cdot \mu(kj|jk, E) \cdot V_{j1}. \end{aligned} \quad (3.6b)$$

Multiplying expression (3.6b) on the left-hand side by $e^{-i\mathbf{q} \cdot \mathbf{r}_1}$ (\mathbf{r}_1 position of metal atom 1), summation over the index 1 and replacement of the summation by an integration gives

$$V_0^s(E, \mathbf{q}) = \frac{1 - V_{00}^s(E) \cdot \mu'(\mathbf{q}, E)}{q^2 \cdot \epsilon(E, \mathbf{q})}, \quad (3.7)$$

where we assumed $\mu(kj|jk, E)$ to depend only on $j - k$ as in the bulk of the metal. Note the difference between V_0^s and V^s given by expression (2.15) due to the surface terms.

Using Eq. (3.7) one derives for $V_{00}^s(E)$:

$$V_{00}^s(E) = \frac{V_{00} \left\{ 1 - \int d\mathbf{q} \int_{r>0} d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{[1 - \nu(E)] \cdot \mu'(\mathbf{q}, E)}{\epsilon(E, \mathbf{q}) q^2} \right\} - \int d\mathbf{q} \int_{r>0} d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{[1 - \nu(E)] \mu(\mathbf{q}, E)}{\epsilon(E, \mathbf{q}) q^4}}{1 + \mu(00|00; E) \cdot V_{00} - \int d\mathbf{q} \int_{r>0} d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \left(\frac{\mu'(\mathbf{q}, E)}{\epsilon(E, \mathbf{q}) \cdot q^2} + \frac{\mu'(\mathbf{q}, E) \cdot \mu(\mathbf{q}, E)}{\epsilon(E, \mathbf{q}) q^4} \right)} \quad (3.8)$$

with

$$\mu'(\mathbf{q}, E) = \int d\mathbf{r}_{0j} e^{-i\mathbf{q} \cdot \mathbf{r}_{0j}} \mu(0j|j0, E) \quad (3.9)$$

and

$$1 - \nu(E) \approx \lim_{\mathbf{q} \rightarrow 0} \frac{\epsilon(E, \mathbf{q})}{\epsilon(E, \mathbf{q}) - 1}. \quad (3.10)$$

Evaluation of the integrals (see the Appendix) in Eq. (3.8) gives in the limit $z_0 \rightarrow \infty$, with z_0 being the distance between adsorbate and surface:

$$\begin{aligned} V_{00}^s(E) &= \frac{V_{00} - \frac{1}{2z_0} \left(1 - \frac{E^2}{\omega_{p,s}^2} \right)^{-1}}{1 + \mu(00|00, E) V_{00} - \frac{1}{2z_0} \left(1 - \frac{E^2}{\omega_p^2} \right)^{-1} \mu'(E)}, \end{aligned} \quad (3.11)$$

$\omega_{p,s}$ is the surface plasmon frequency.

Since

$$\sum_{k \neq 0} H_{0k} G_{k0}^0 \sum_{k' \neq 0}^c \ll \sum_{k \neq 0} H_{0k}^2 G_{kk}^0 \quad (3.12)$$

expression (3.3) simplifies for G_{00} to

$$G_{00} = \frac{1}{G_{00}^{0-1} - \sum_{00}^c(E)} \quad (3.13)$$

with

$$\sum_{00}^c(E) = i \int dE V_{00}^s(E) G_{00}^s(E) - V_{00} n_0^\sigma. \quad (3.14)$$

n_0^σ is the electron occupation of an electron with spin σ at position 0. As discussed by Hedin and Lundquist,¹² the integration in Eq. (3.14) can be split into two parts: one term due to the poles in $G_{00}(E)$ giving the screened exchange term, the other due to the denominator of V_{00}^s giving the Coulomb-hole term. Screening of the exchange term gives a repulsive contribution, which is compensated by an attractive term due to the Coulomb hole interaction. As long as $\mu(00|00, E) V_{00}$ is small, the screened exchange contribution becomes

$$V_{\text{exch}}^{s,\sigma} = \frac{1}{2z_0} \int_{-\infty}^{E_F} dE' \left(1 - \frac{2(E - E')^2}{\omega_{s,p}^2} \right)^{-1} n_0^\sigma(E'). \quad (3.15)$$

This is the contribution considered by Kranz and Griffin.⁵ The Coulomb-hole contribution becomes

$$\begin{aligned} V_{\text{Coul. hole}}^{s,\sigma} &= -\frac{\omega_p}{2z_0} \cdot \text{Re } G_{00}^\sigma(E + \omega_p) \\ &\quad \times \frac{\mu(00, 00, \omega_p) V_{00}}{1 + \mu(00, 00, \omega_p) V_{00}}. \end{aligned} \quad (3.16)$$

IV. THE IMAGE POTENTIAL

The matrix element for the electrostatic potential at position 0 of the adsorbate becomes

$$\langle \psi_0 | V_{\text{eff}}^{\text{HF}} | \psi_0 \rangle = \frac{1}{2} V_{00} n_0 + \sum_{i \neq 0} \frac{1}{|r_0 - r_i|} \Delta n_i. \quad (4.1)$$

$V_{\text{eff}}^{\text{HF}}$ is the Hartree potential at position 0 corrected for the electron self-energy at position 0.

To lowest order in Δn_0 , the induced charges at positions i in the metal are the solutions of the set of linear equations:

$$\Delta n_i = - \sum_{m \neq n} \lambda_{im} \frac{1}{|r_m - r_n|} \Delta n_n - \sum_{m \neq 0} \lambda_{im} \frac{1}{|r_m - r_0|} \Delta n_0 \quad (4.2a)$$

with

$$\lambda_{im} = - \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \sum_n G_{in}(E) \frac{1}{|r_n - r_m|} G_{nm}(E). \quad (4.2b)$$

For large values of the indices the summation in Eq. (4.2) may be replaced by integrals. Fourier transformation of the resulting expressions gives

$$\Delta n(q) = - \frac{l_s^{-2}}{q^2 + l_s^{-2}} \Delta n_0 \quad (4.3)$$

with

$$l_s^{-2}(q) = - \frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \int dr_{im} e^{-iq \cdot r_{im}} G_{im}(E) G_{mi}(E). \quad (4.4)$$

It is of interest to note the close relationship between the static l_s and the dynamic λ^{-1} screening length [see Eq. (2.16)]. At the surface, expressions (4.2) and (4.3) have to be solved with the proper boundary conditions. The expression to evaluate for the induced potential at position 0 becomes

$$V_{\text{ind}} = \sum_k \frac{e^2}{|r_0 - r_k|} \Delta n_k = - \int_{r>0} dq \int dr \frac{l_s^{-2} e^{iq_z \cdot z_0}}{q^2 \cdot (q^2 + l_s^{-2})} \Delta n_0. \quad (4.5)$$

In the Appendix it is shown that this expression simplifies to

$$\lim_{z_0 \rightarrow \infty} V_{\text{ind}}(z_0) = - \frac{1}{2z_0} \Delta n_0, \quad (4.6a)$$

$$\lim_{z_0 \rightarrow 0} V_{\text{ind}}(z_0) = - \frac{1}{2l_s} \Delta n_0. \quad (4.6b)$$

The latter is the well known result of Gomer and Swanson.¹³ Expressions (4.6) differ by a factor of 2 from the image potential. This is because we have ignored the repulsive interaction energy term due to the interaction of the induced metal charges

$$E_{\text{rep}}^{\text{met}} = \frac{1}{2} \int d\mathbf{q} \cdot \frac{1}{q^2} \Delta n(\mathbf{q}) \cdot \Delta n(\mathbf{q}) \quad (4.7a)$$

which becomes for large values of z_0 :

$$\frac{1}{4z_0} \Delta n_0^2. \quad (4.7b)$$

If one adds the interaction with the nuclei to the interaction with the electrons as demonstrated later, one finds at large distances for the image energy the classical electrostatic result.

V. CALCULATED RESULTS

Using Eqs. (3.15) and (3.16) the effect of coupling with bulk and surface plasmons on the bond strength can be calculated. Here we present some results of model calculations using the Newns-Anderson formalism. Details of the calculations are similar to those discussed elsewhere.¹⁴ If one includes electron-electron repulsion on the adsorbate and between the adsorbate and neighboring atoms one derives an expression for the adsorption energy for an hydrogen-type adsorbate:

$$E_{\text{ads}} = \Delta E - V_{00} \cdot n_0^\sigma \cdot n_0^{\sigma'} - \sum_{\sigma} |P_{01}^\sigma|^2 V_{01} + \frac{1}{2z_0} \cdot \Delta n_0 + \frac{1}{4z_0} \cdot \Delta n_0^2, \quad (5.1a)$$

$$\Delta E = \sum_{\sigma} \left\{ \frac{1}{\pi} \int_{E_{\text{min}}}^{E_F} \eta^\sigma(E) dE + \sum_k (E_k^\sigma - E_F) - (\alpha_0 - E_F) \right\}, \quad (5.1b)$$

$$\tan \eta^\sigma(E) = \frac{\Gamma^\sigma(E)}{\alpha_0^{\sigma'} + \Lambda^\sigma(E) - E} \quad (5.1c)$$

with E_k^σ representing the discrete roots of $\alpha_0^{\sigma'} + \Lambda^\sigma(E) - E$ when $\Gamma^\sigma(E) = 0$,

$$\Gamma^\sigma = \beta'^{\sigma 2} \text{Im} \left[\alpha_m - E - \frac{Z^s}{2Z} (E - \alpha_m \pm i\sqrt{4Z\beta^2 - (E - \alpha_m)^2})^{-1} \right]^{-1}, \quad 4Z\beta^2 > (E - \alpha_m)^2 \quad (5.1d)$$

$$\Lambda^\sigma = \beta'^{\sigma 2} \text{Re} \left[\alpha_m - E - \frac{Z^s}{2Z} (E - \alpha_m \pm \sqrt{(E - \alpha_m)^2 - 4Z\beta^2})^{-1} \right]^{-1}, \quad 4Z\beta^2 < (E - \alpha_m)^2, \quad (5.1e)$$

$$\Lambda^\sigma = \beta'^{\sigma 2} \text{Re} \left[\alpha_m - E - \frac{Z^s}{2Z} (E - \alpha_m \pm i\sqrt{4Z\beta^2 - (E - \alpha_m)^2})^{-1} \right]^{-1}, \quad 4Z\beta^2 > (E - \alpha_m)^2$$

$$\alpha_0^{\sigma'} = \alpha_0 - \frac{1}{2z_0} \Delta n_0 + U n_0^{\sigma'} + V_{\text{exch}}^s + V_{\text{Coul. hole}}^s. \quad (5.1f)$$

In Eqs. (5.1d) and (5.1e) the $-$ sign is used when $E - \alpha_m > 0$, and the $+$ sign when $E - \alpha_m < 0$. We have used the Bethe lattice approximation for a lattice consisting of a single valence electron band. α_m is the Coulomb energy integral of the metal atomic orbitals and β their overlap energy intergral. Z_s equals the number of metal atoms that are nearest neighbors of the metal atom interacting with the adsorbate excluding the metal atoms that interact with the adsorbate. $Z + 1$ equals the effective number of bulk neighbor atoms. E_{\min} is the bottom of the valence band, E_F the Fermi level. α_0 is the adsorbate orbital energy containing one electron before adsorption. V_{00} is the one-center repulsion integral at the adsorbate, V_{0i} is the two-center repulsion integral

between adsorbate and nearest neighbor metal atom. P_{01}^σ is the corresponding bond order. β' is the overlap energy matrix element between adsorbate and surface atom orbital, β'^σ the corresponding Hamiltonian matrix element:

$$\beta'^\sigma = \beta' - P_{01}^\sigma V_{01}. \quad (5.2)$$

Since α_0^σ and β'^σ depend on the electron density, a self-consistent method is used. The term depending explicitly on $1/2z_0$ accounts for the static image energy.

Approximate expressions for V_{exch}^σ and $V_{\text{Coul. hole}}$ are used:

$$V_{\text{exch}}^{\sigma} \approx \frac{1}{2z_0} \frac{\frac{1}{2}\omega_p^2}{\frac{1}{2}\omega_p^2 + (\beta'^{\sigma 2}/2\sqrt{Z^s\beta})^2} n_0^\sigma, \quad (5.3a)$$

$$V_{\text{Coul. hole}} \approx -\frac{1}{2z_0} \frac{\omega_p^2}{\omega_p^2 + (\beta'^{\sigma 2}/2\sqrt{Z^s\beta})^2}. \quad (5.3b)$$

In Figs. 1(a) and 1(b), E_{ads}/β' and $(n_0^\sigma - n_0^{\sigma'})$ are plotted as a function of β' for two values of z_0 . Parameters have been chosen such that $n_0^\sigma + n_0^{\sigma'} \approx 1$. Table I shows that the results do not depend strongly on the value of ω_p .

As in the Anderson model,¹⁵ $n_0^{\sigma'} = n_0^\sigma$, if $\beta' \gtrsim \beta$. For these values the correlation energy is found to be maximum. Clearly this is a coincidence, since this transition point is independent of ω_p .

VI. DISCUSSION

In order to compare our result with those by Hewson and Newns,⁴ one has to study the expressions for α_0^σ , the Hamiltonian matrix element at the adsorbate. One finds

$$\alpha_0^\sigma = \alpha_0 + \left(V_{00} - \frac{1}{2z_0}\right) n_0^{\sigma'}, \quad |\Gamma'^\sigma|/\omega_p \ll 1 \quad (6.1a)$$

$$= \alpha_0 + V_{00} n_0^{\sigma'} + \frac{1}{2z_0} (1 - n_0^\sigma - n_0^{\sigma'}), \quad |\Gamma'^\sigma|/\omega_p \gg 1, \quad (6.1b)$$

$$\Gamma'^\sigma = \frac{\beta'^{\sigma 2}}{2\sqrt{Z^s\beta}}. \quad (6.1c)$$

For weak chemisorption the electron-electron repulsion is found to be screened by $-(1/2z_0) n_0^{\sigma'}$. This is an effect discussed by many authors in the context of photoemission^{4,5,16}

TABLE I. Effect of plasmon frequency on chemisorption energy; same parameters as in Fig. 1; $z_0 = 2.1 \text{ \AA}$.

Tabulated: E_{ads}/β'						
β'/ω_p	0.0	3	9	11	13.6	30
-0.1	0.0005	0.002	0.002	0.001	0.02	0.02
-0.2	0.014	0.03	0.03	0.032	0.03	0.03
-0.6	0.08	0.13	0.13	0.13	0.13	0.13
-1	0.15	0.26	0.23	0.23	0.23	0.22
-2	0.35	0.65	0.66	0.67	0.67	0.76
-3	0.71	0.84	1.05	1.06	1.07	1.08
-5	1.15	1.17	1.30	1.31	1.32	1.37
-10	1.52	1.52	1.53	1.54	1.55	1.60
-30	1.81	1.81	1.81	1.81	1.81	1.82

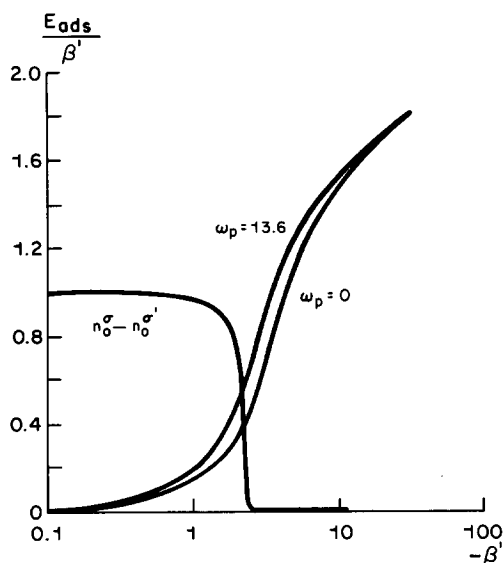


FIG. 1a

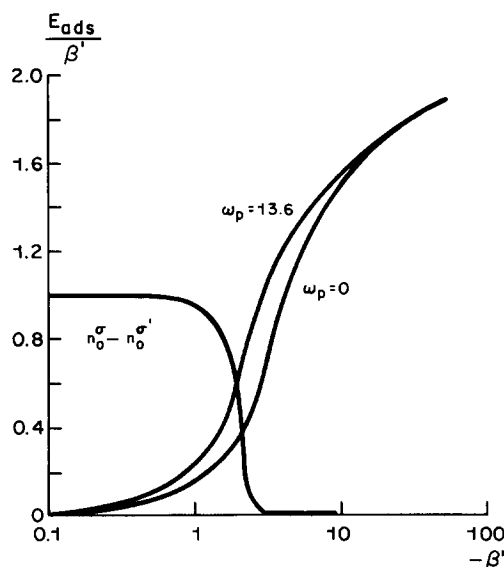


FIG. 1b

FIG. 1. Effect of plasmon coupling on chemisorption energy. $n_0^\sigma - n_0^{\sigma'}$ and E_{ads}/β' as a function of β' . $Z = 9$, $\beta = -2$, $U_0 = 13.6$, $\alpha_0 = -5.6$, $Z_s = 6$, $E_F = 0.0$, $U_{01} = 6$. (a) $z_0 = 4.2 \text{ \AA}$, (b) $z_0 = 2.1 \text{ \AA}$.

and demonstrated here to be valid only when $|\Gamma'| \ll \omega_p$. Under these conditions the contribution to the correlation energy is dominated by the Coulomb hole interaction, as clearly discussed by Inkson.¹⁷

In this limit the calculations show that the overall effect on the bond energy is negligible in the absence of charge transfers, in agreement with findings by Kranz and Griffin.⁵ The screened exchange and Coulomb-hole contribution appear to cancel, because spin polarization annihilates the probability to find an electron of opposite spin at the adsorbate. As a consequence the electron-electron interaction at the adsorbate becomes negligible.

Expressions (6.1b) show that also in the opposite case of strong chemisorption, correlation effects disappear. This is a well-known result from quantum chemical theory.¹⁸ Correlation effects become negligible when covalent bonding effects become large with respect to the electron-electron interactions.

Since the tunneling time τ of the adsorbate is inverse to Γ' , the weak adsorption limit is equivalent to the adiabatic limit where the tunneling time is very long compared to the plasmon frequency period T . In this limit the electrons in the metal adjust to the electron motion at the adsorbate and screening is complete. The static limit $\tau \ll T$ is equivalent to the strong chemisorption limit. Then the tunneling time is so short that the electrons in the metal cannot follow the motion of adsorbate electrons and hence the correction to the Hartree-Fock result vanishes.

The plasmon interaction reaches its maximum value if $\tau \sim T$, when tunneling frequency and plasmon frequency are at resonance.

Of interest is our finding of important effects in the intermediate range. Previously¹⁴ we found for H coordinated to the s band of Pt: $\beta'/\beta \approx 0.7$. So considerable effects on the bond strength may be expected ($\sim 20\%$). However, as follows from the weak Γ' dependence, differences in coordination energy will be very slightly affected. It is of interest to note that the effect of nonlocality on the surface energy has been found to be of a similar order of magnitude.¹⁹ We did not explicitly account for the screening of V_{00} due to V_{01} found in the Hartree-Fock part of the Hamiltonian.²⁰ Since Eq. (5.2) depends explicitly on V_{01} the effect has been implicitly incorporated. A limitation of our treatment is the absence of van der Waals terms in the expression for the bond energy. These will become of interest at low values of Γ'/ω_p .

APPENDIX

We will evaluate expression (4.5) in cylinder symmetry

$$\Delta n(q_z \cdot \mathbf{q}) = \int_0^\infty dz \int_0^\infty r dr \int_0^{2\pi} d\phi e^{-iq_z \cdot z - iq' \cdot r} \Delta n(z, \mathbf{r}) \quad (\text{A1})$$

with \mathbf{q} and \mathbf{r} being vectors parallel to the surface plane. Evaluation of the integrals gives

$$\Delta n(q_z \cdot \mathbf{q}) = -\frac{l_s^{-2}(\mathbf{Q})}{q_z^2 + q^2 + l_s^{-2}(\mathbf{Q})} e^{iq_z \cdot z_0} \quad (\text{A2})$$

with $q = |\mathbf{q}|$ and q_z , components of \mathbf{Q} . z_0 is the position of the adsorbate with respect to the surface:

$$\Delta n_k = \int_0^\infty dq_z \int_0^\infty q dq \int_0^{2\pi} d\phi l_s^{-2}(\mathbf{Q}) \times \frac{e^{iq_z(z_k + z_0)}}{q_z^2 + q^2 + l_s^{-2}(\mathbf{Q})} e^{iq' \cdot r_k} \Delta n_0 \quad (\text{A3})$$

$$\simeq \pi \int_0^{2\pi} d\phi \int_0^\infty q dq l_s^{-2}(\mathbf{Q}) \times \frac{e^{-\sqrt{q^2 + l_s^{-2}}(z_k + z_0)}}{\sqrt{q^2 + l_s^{-2}}(\mathbf{Q})} e^{iq' \cdot r_k} \Delta n_0, \quad (\text{A4})$$

the induced potential is

$$V_{\text{ind}} = \sum_k \frac{e^2}{|r_0 - r_k|} \Delta n_k \quad (\text{A5})$$

$$\simeq \frac{\pi}{2\pi^3} l_s^{-2} \int_{r>0} dr \int d\mathbf{Q} \frac{e^{-iq_z(z+z_0)} e^{-iq' \cdot r}}{q_z^2 + q^2} * \int_0^{2\pi} d\phi \int_0^\infty dq e^{iq' \cdot r} \frac{e^{-\sqrt{q^2 + l_s^{-2}}(z+z_0)}}{\sqrt{q^2 + l_s^{-2}}} * \Delta n_0$$

$$= -l_s^{-2} \int_0^\infty dq \frac{1}{q + \sqrt{q^2 + l_s^{-2}}} * \frac{e^{-(q + \sqrt{q^2 + l_s^{-2}})z_0}}{\sqrt{q^2 + l_s^{-2}}} * \Delta n_0. \quad (\text{A6})$$

Partial integration gives

$$\lim_{z_0 \rightarrow \infty} V_0^{\text{ind}}(z_0) = -\frac{1}{2z_0} \Delta n_0,$$

$$\lim_{z_0 \rightarrow \infty} V_0^{\text{ind}}(z_0) = -\frac{\pi}{l_s} \Delta n_0.$$

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