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"Energy Transfer in Interactions with
Surfaces and Adsorbates"
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"Linear Electronic Response of Surfaces and Adsorbates"

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Linear electronic response of surfaces & adsorbates

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General references:

1) D. M. Newns, Phys. Rev. B1, 3304 (1970).
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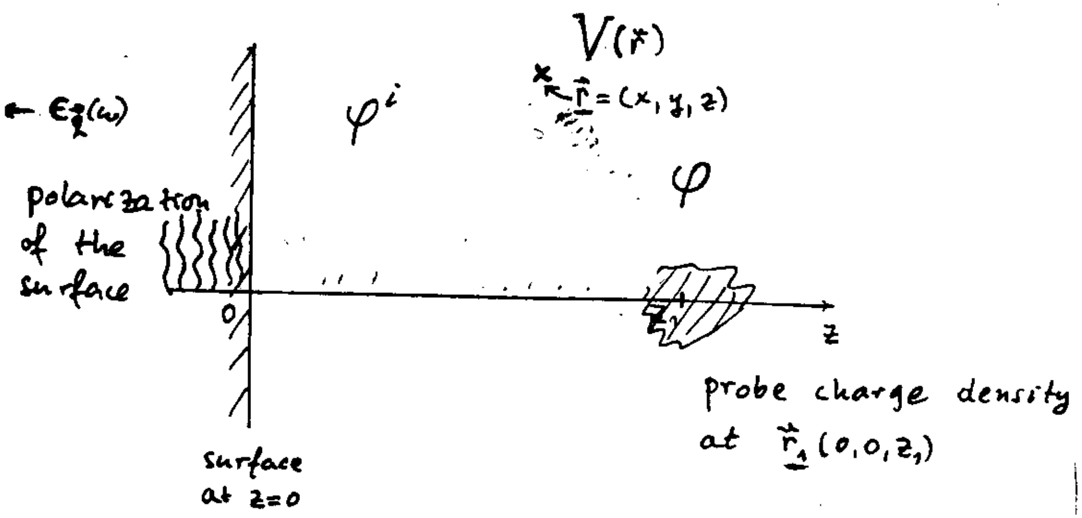
C)

Surface response function for semi-infinit electron gas



Total selfconsistent potential ar $\vec{r}$ due to the probe charge density at $\vec{r}_1$:

$$\boxed{V(\vec{r}) = \varphi(\vec{r}) + \varphi^i(\vec{r})} \qquad \text{(Three-body interaction)} \qquad (II.2$$

where:

$\varphi(\vec{r})$ ... direct applied potential in the absence of surface

$\varphi^i(\vec{r})$ .... induced potential due to the

C 1.

Quantum image theorem

Since the system (i.e. the surface) is translationally invariant in (x,y) direction along the surface, the potential $V(\vec{r})$ and its constituents may be Fourier-transformed in terms of

$\underset{\sim}{Q}$ ... wave vector paralel to the surface

ω ... frequency of applied "direct" potential

Newns [PRB 1, 3304 (1970)] showed that in $(\underset{\sim}{Q}, z, \omega)$ space the following quantum analog of the image theorem holds:

$$\boxed{V_{\underset{\sim}{Q}}(z,\omega) = \varphi_{\underset{\sim}{Q}}(z,\omega) + \varphi_{\underset{\sim}{Q}}(-z,\omega)\frac{1-\epsilon_{\underset{\sim}{Q}}(\omega)}{1+\epsilon_{\underset{\sim}{Q}}(\omega)}}_{z>0} \qquad (\text{II}.21)$$

where

$\varphi_{\underset{\sim}{Q}}(-z,\omega)$ .... potential reflected at the surface

$\epsilon_{\underset{\sim}{Q}}(\omega)$ .... Two dimensional analog of the bulk dielectric function $\epsilon_{\underset{\sim}{q}}(\omega)$ with the property:

$$\lim_{Q\to 0} \epsilon_Q(\omega) = \lim_{q\to 0} \epsilon_q(\omega)$$

where $\vec{q} = (\underset{\sim}{Q}, q_z)$

The knowledge of

C. 2) Definition of the surface response function

The causal properties of $\epsilon_q(\omega)$, and, hence of $\epsilon_Q(\omega)$, enable the identification and the definition of the surface response function $R_{\underset{\sim}{Q}}(\omega)$:

Def.

$$\boxed{R_Q(\omega) = \frac{1-\epsilon_Q(\omega)}{1+\epsilon_Q(\omega)}} \qquad (\text{II}.22)$$

[Gumhalter & Newns; Phys. Lett 53A, 137 (1975); Gumhalter J. Phys. (Paris) 38, 1117 (1977); Gumhalter, Progr. Surface Sci 15, 1 (1984)]

The analytic (causal) properties of $\epsilon_Q(\omega)$ and $R_Q(\omega)$ can be exploited to write $R_Q(\omega)$ in the spectral or Lehman representation

$$\boxed{R_{\underset{\sim}{Q}}(\omega) = \int_0^\infty d\omega' \, S_{\underset{\sim}{Q}}(\omega')\left(\frac{1}{\omega-\omega'+i\delta} - \frac{1}{\omega+\omega'+i\delta}\right)} \qquad (\text{II}.23)$$

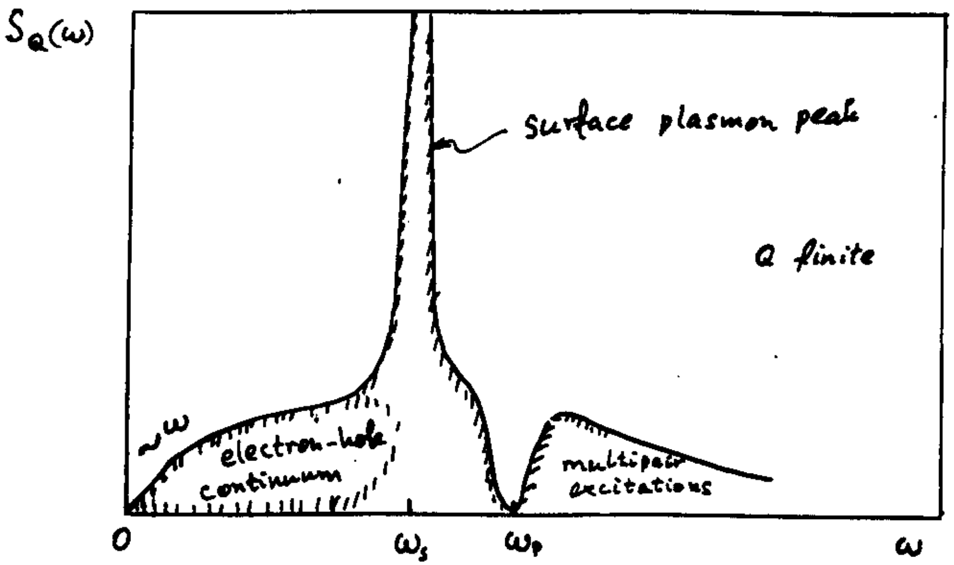
where the spectrum of the surface excitation is obtained as:

$$S_Q(\omega) = -\frac{2}{\pi}\frac{\text{Im}\,\epsilon_Q^{-1}(\omega)}{[1+\text{Re}\,\epsilon_Q^{-1}(\omega)]^2 + [\text{Im}\,\epsilon_Q^{-1}(\omega)]^2} \qquad (\text{II}.24)$$

$S_Q(\omega)$ may also be identified with the dynamic form factor of the semi-infinite electron gas.

General behaviour of $S_Q(\omega)$ for free electron gas (free electron metal surfaces)

$S_Q(\omega)$ = surface excitation spectrum comprises electron-hole continuum + collective mode (surface plasmon). This holds true in any model of the surface!



C.3.

Properties of the surface response function R_Q and the surface excitation spectrum $S_Q(\omega)$

a) Sum rules or moments of the spectrum $S_Q(\omega)$

(i) Perfect screening sum rule and surface screening charge density:

- Response to static external perturbation: Using spectral representation we get:

$$R_Q(\underline{\underline{\omega=0}}) = -2\underbrace{\int_0^\infty d\omega' \frac{S_Q(\omega')}{\omega'}}_{\mu_{-1}(Q)} \qquad (\text{II}.25)$$

Perfect screening sum rule reads

$$\boxed{\lim_{Q\to 0} \mu_{-1}(Q) = \int_0^\infty d\omega' \frac{S_Q(\omega')}{\omega'} = \frac{1}{2} + Q z_c + O(Q^2)} \qquad (\text{II}.26)$$

where

$$z_c = \frac{\int z\,\delta\rho(\vec r)\,d^3r}{\int \delta\rho(\vec r)\,d^3r}$$

.... centre of mass of the screening charge $\delta\rho(\vec r)$ induced at the surface.

$\delta\rho(\vec r)$ and z_c available from the

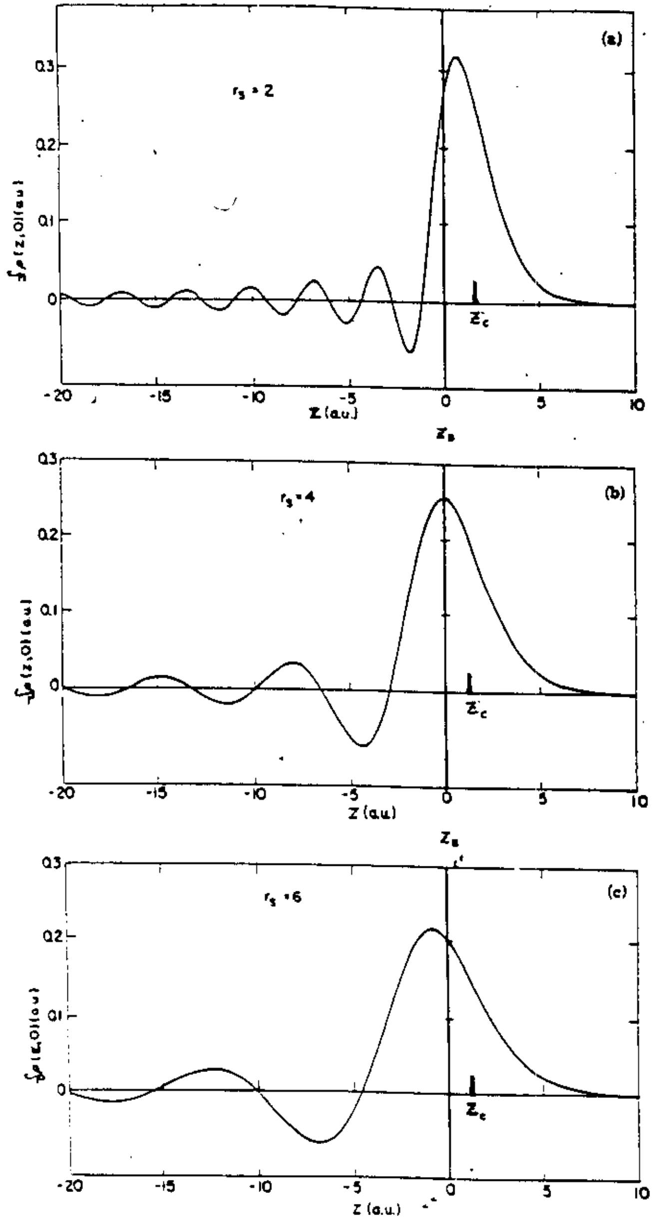


FIG. .. Profiles of induced surface charge density $\delta\rho(z,0)$. z and ρ are measured in atomic units ($|e| = m = \hbar = 1$); the atomic unit of length is 0.529 Å. Note that $\rho(z;0)$ satisfies the normalization condition Eq. (3.3). r_s characterizes the bulk densities ($\frac{4}{3}\pi r_s^3 = \rho_e^{-1}$, with ρ_e the bulk electronic charge density, in atomic units). The edge of the uniform positive-charge background, Z_B, is taken at the origin. Z_0 the center of mass of $\delta\rho(z;0)$, is shown in the text to be the effective location of the metal surface. (These density distributions are the same as those given in Ref. 2, except for some very small differences arising from use in the present computation of somewhat weaker fields.)

interior ← $Z_B=0$ → exterior

α

(ii) Surface f-sum rule

(Conservation of the number of electrons in the system)

- Response to rapidly oscillating external perturbation:

Using again the spectral representation we get:

$$\lim_{\omega\to\infty} R_Q(\omega) = \frac{2}{\omega^2}\underbrace{\int_0^\infty \omega' S_Q(\omega')\,d\omega'}_{\mu_1(Q)}$$

$\mu_1(Q)$ can be calculated using the 2-dimensional analog of the continuity equation [Gumhalter, J. Phys (Paris) 38, 1117 (1977); Progress in Surf. Sci. 15, 1 (1984)]
Phys. Lett. 53A (1975) 137

$$\boxed{\mu_1(Q) = \int_0^\infty \omega' S_Q(\omega')\,d\omega' = \frac{2\pi Q}{m}\int e^{2Qz}\rho(z)\,dz} \qquad (\text{II}.27)$$

m... electron mass

$\rho(z)$... profile of the charge density of the metal accross the surface (available e.g. for free electron metals modelled by Jellium surfaces).

$\rho(z)$ is a property of the unperturbed system!

Comparison of surface density profiles $\rho(z)$ obtained within different models of surface

1 DIELECTRIC RESPONSE OF A SEMI-INFINITE ELECTRON GAS 3305

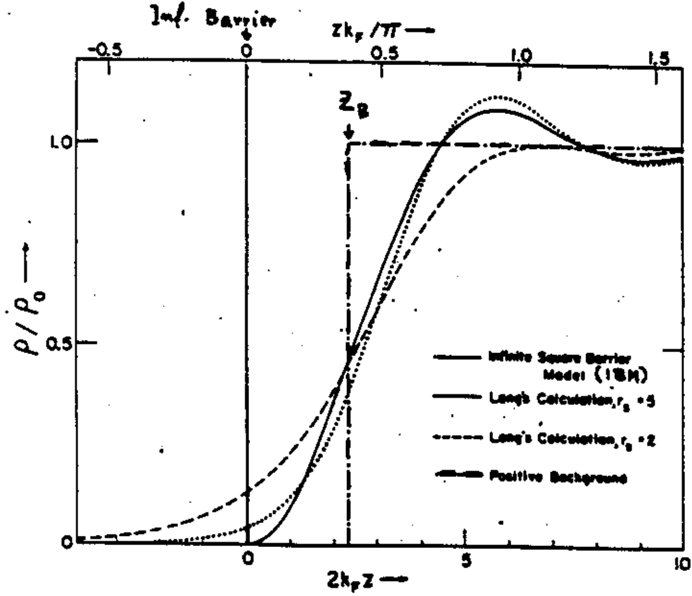


FIG. . Charge density of electron gas at metal surface. Solid line refers to infinite square barrier in region $Z<0$, assuming free electrons, and remaining curves to self-consistent calculations of Lang (see text for details). ρ_0 is density in interior of metal. Unit π/k_F equals one half-Fermi wavelength.

exterior of the solid ←

↓ z_B

→ interior of the solid

C. 4.

Long wavelength limit of the surface response function $R_Q(\omega)$

For many practical purposes it is sufficient to know the long wavelength limit $(Q \to 0)$ of the surface response function $R_Q(\omega)$.

In the long wavelength limit one can conveniently write (Feibelman, Progress in Surf. Sci. 12, 287 (1982)):

$$\boxed{R_Q(\omega) = R_0(\omega)\left[1 + 2Q\, d_{IP}(\omega)\right] + O(Q^2)} \qquad (\text{II}.28)$$

where:

$$R_0(\omega) = R_{Q=0}(\omega),$$

$d_{IP}(\omega)$ ... frequency dependent complex centroid of the image charge (Feibelman, ibid) defined as:

$$\boxed{d_{IP}(\omega) = \frac{d_{\parallel}(\omega) + \epsilon_0(\omega)\, d_{\perp}(\omega)}{\epsilon_0(\omega) + 1}.} \qquad (\text{II}.29)$$

Here

$\epsilon_0(\omega) = \lim_{Q\to 0} \epsilon_Q(\omega)$ .... bulk dielectric function for and

$$d_\perp(\omega) = \frac{\int dz\; z\; \delta\rho(z,0,\omega)}{\int dz\; \delta\rho(z,0,\omega)} = z_c(\omega)\,, \qquad (\underline{II}.30)$$

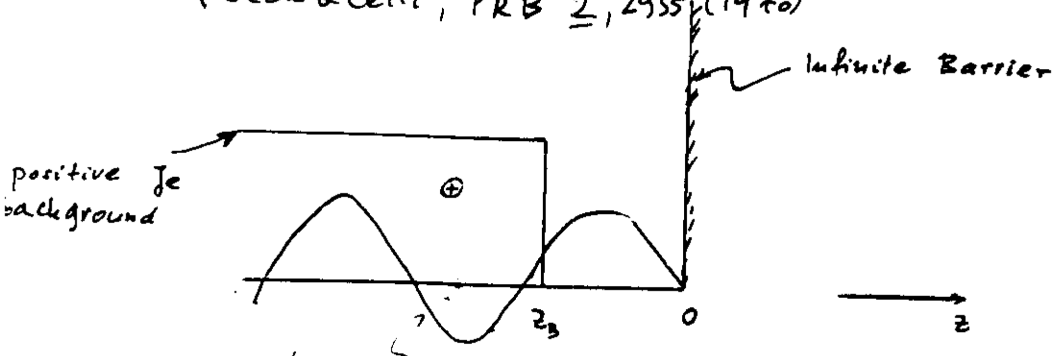
$$d_\parallel(\omega) = \frac{\int dz\; z\; \left(\frac{d\; j_\parallel(z,0,\omega)}{dz}\right)}{\int dz\; \left(\frac{d\; j_\parallel(z,0,\omega)}{dz}\right)}\,. \qquad (\underline{II}.31)$$

where $\delta\rho(z,\underset{\sim}{Q},\omega)$ and $j_\parallel(z,\underset{\sim}{Q},\omega)$ are 2-dimensional Fourier transforms of the induced charge density $\delta\rho(\underset{\sim}{r},\omega)$ and the current density $j_\parallel(\underset{\sim}{r},\omega)$ parallel to the surface.

Model calculations of $R_Q(\omega)$ and $S_Q(\omega)$

$\boxed{a)}$ Analitically solvable Infinite Barrier Model

(IBM: Newns PRB $\underline{1}$, 3304 (1970)
Beck & Celli, PRB $\underline{2}$, 2955 (1970))



Here, $R_{\underset{\sim}{Q}}(\omega)$ is obtained by calculating first the surface excitation spectrum $S_Q(\omega)$ from eq. $\underline{II}$.24. and then taking its Hilbert transform given by eq. $\underline{II}$.23. Thus, one finds (Gumhalter, J. Phys. (Paris) $\underline{38}$, 1117 (1977); Progress in Surf. Sci. $\underline{15}$, 1 (1984)):

$$\lim_{\substack{Q\to 0\\ \omega\to 0}} S^{RPA}_{\underset{\sim}{Q}}(\omega) = 2\,\frac{\omega Q}{\pi\sqrt{3}\,\omega_p k_{TF}}\left(\ln\frac{2k_{TF}}{Q} - \frac{1}{2}\right) - \frac{2}{3\pi}\left(\frac{\omega}{\omega_p}\right)^2 + \cdots \qquad (\underline{II}.32)$$

$$\lim_{\substack{Q\to 0\\ \omega\to \omega_s}} S_Q(\omega) = \frac{\omega_s}{2}\,\delta(\omega-\omega_s) + O(Q) \qquad (\underline{II}.33)$$

where:

$\omega_p = \frac{4\pi e^2 N}{m}$ … bulk plasmon frequency

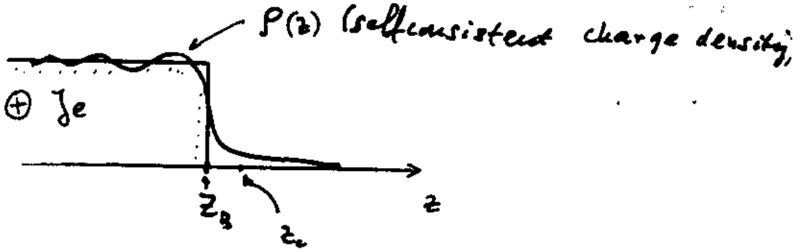
$\omega_s = \frac{\omega_p}{\sqrt{2}}$

k_{TF} … Thomas-Fermi wave vector

N … number of electrons per unit volume

$\left.\begin{matrix} e \\ m \end{matrix}\right\}$ electron $\left\{\begin{matrix} \text{charge} \\ \text{mass} \end{matrix}\right.$

b) Self-consistent Jellium model of a surface



For a flat Je surface

$$d_{\parallel}(\omega) = z_B$$

and the problem of calculating $R_a(\omega)$ for $a \to 0$ reduces to finding $d_\perp(\omega)$.

(i) The Ansatz of Zaremba and Kohn for $d_\perp(\omega)$

Using the sum rules (II.26.) and (II.27.) one may determine $R_a(0)$ and $R_a(\omega \to \infty)$ in the limit $a \to 0$. This allows introducing the Ansatz:

$$d_{IP}^{zk}(\omega) = \frac{z_B\,\omega^2 - z_c\,\omega_s^2}{\omega^2 - \omega_s^2} \qquad (\underline{II}.\,34.)$$

which gives $R_a(\omega)$ which obeys both sum rules. Hence:

$$d_\perp^{zk}(\omega) = \frac{z_B\,\omega^2 - z_c\,\omega_p^2}{\omega^2 - \omega_p^2} \qquad (\underline{II}.\,35.)$$

c.f. Zaremba e Kohn Phys. Rev. B 13, 2270 (1976)

(ii) The Ansatz of Persson and Zaremba

By studying analytic properties of $d_\perp(\omega)$, Persson & Zaremba (Phys. Rev. B 30, 5669 (1984)) have arrived at a sum rule for $d_\perp(\omega)$:

$$\boxed{\int_{-\infty}^{\infty} \frac{d\omega}{\pi}\,\omega\,\mathrm{Im}\,d_\perp(\omega) = \omega_p^2\,\lambda} \qquad (\underline{II}.\,36.)$$

and the low frequency behaviour:

$$\lim_{\omega \to 0} \mathrm{Im}\,d_\perp(\omega) = \frac{\bar{\xi}}{k_F}\,\frac{\omega}{\omega_p} \qquad (\underline{II}.\,37.)$$

where:

$$\lambda = \int_{z_B}^{\infty} dz\;\bar{\rho}_0(z) = \int_{-\infty}^{z_B} dz\,[1 - \bar{\rho}_0(z)]$$

and

$\bar{\rho}_0(z) = \rho_0(z) / \bar{\rho}$
k_F ... Fermi wave vector
$\bar{\xi}$ ... dimensionless parameter which depends on the electron density.

Ansatz in accord with the sum rule (II. 36.):

$$d_\perp^{PZ}(\omega) = \frac{z_B\,\eta\,\omega^2 - z_c\,\omega_p^2}{\eta\,\omega^2 - \omega_p^2} \qquad (\underline{II}.\,38.)$$

with

$\eta = z\ /\lambda$

The corresponding

$$d_{IP}^{pz}(\omega) = \frac{z_B + \epsilon_0(\omega)\, d_\perp^{pz}(\omega)}{\epsilon_0(\omega)+1}$$

although exhibiting two pole behaviour, nevertheless satisfies the perfect screening and surface f-sum rule when substituted into $R_a(\omega)$,

(iii) Time dependent density functional approach

Using the density functional approach Liebsch was able to calculate $d_\perp(\omega)$ numerically (Phys. Rev. B 33, 7249(1986)) and compare these results with two former Ansätze:

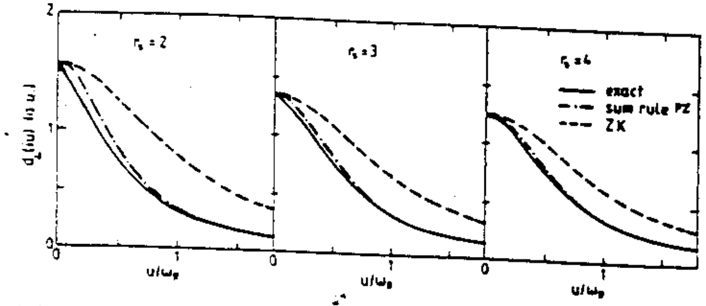
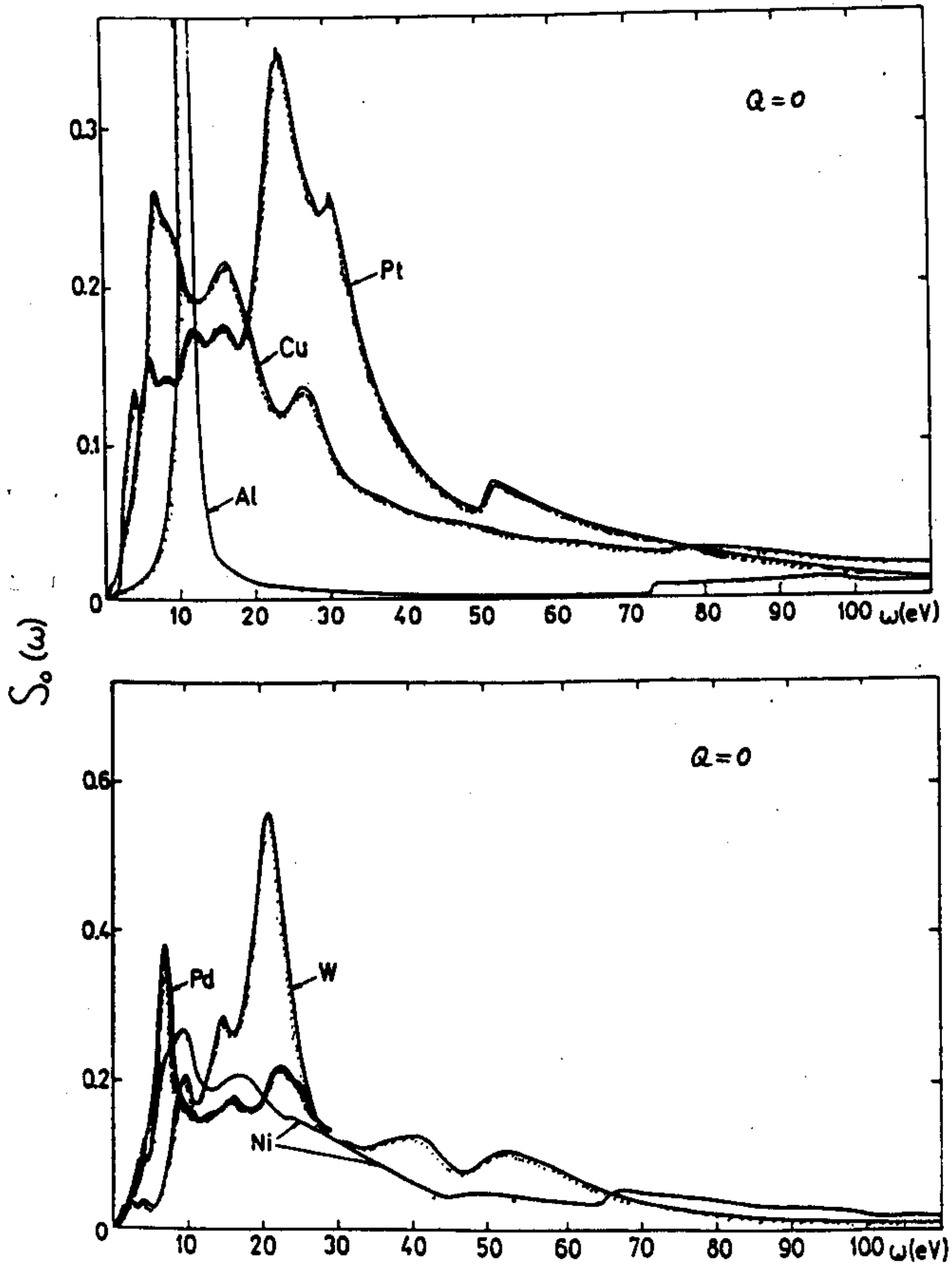


FIG. Centroid of induced charge for several jellium surfaces

Long wavelength limit of the surface excitation spectrum of real metals



Lovrić and Gumhalter PRB 38 (1988) 10323

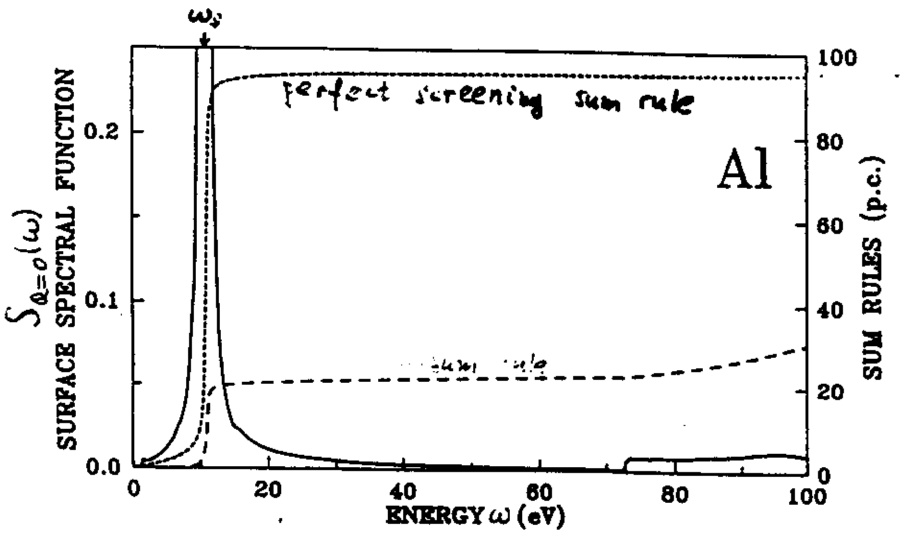


Figure 4.3a: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF ALUMINIUM. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of respective theoretical values.

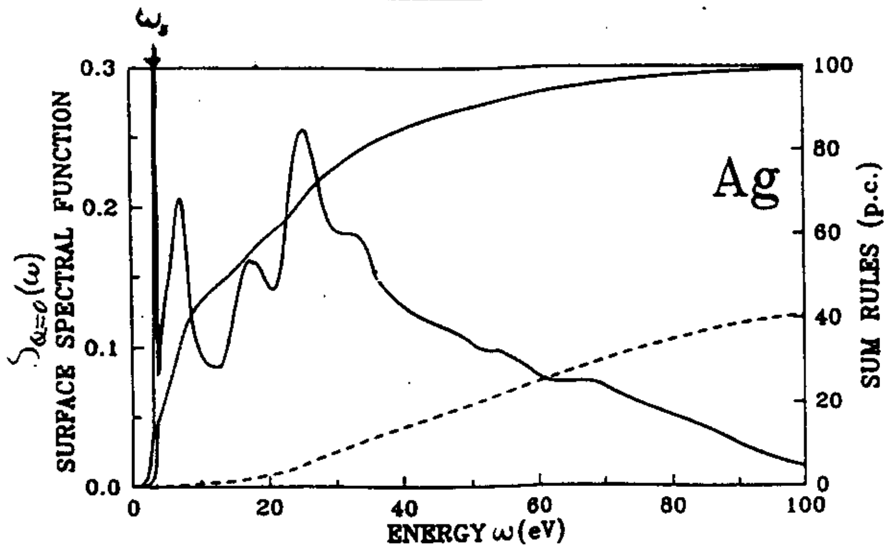


Figure 4.3d: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF SILVER. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in

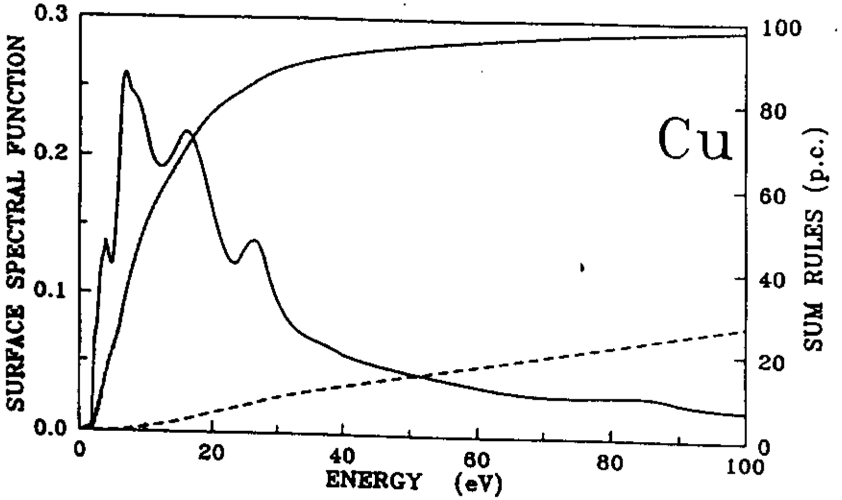


Figure 4.3b: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF COPPER. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of respective theoretical values.

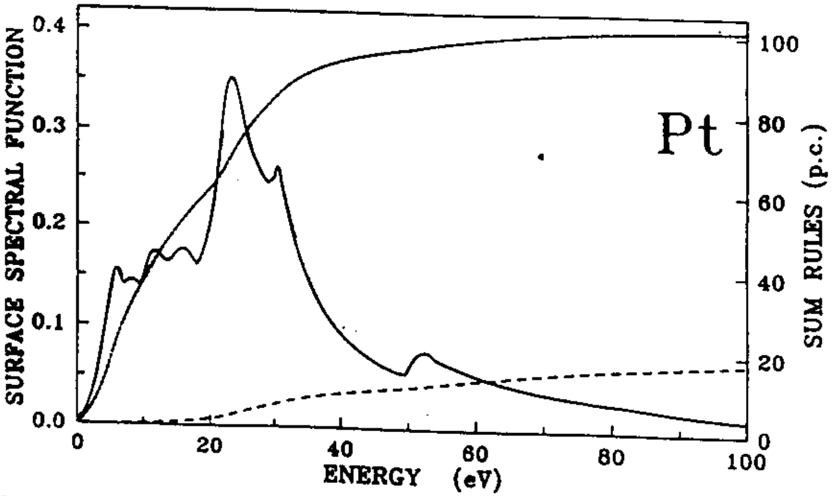


Figure 4.3c: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF PLATINUM. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of respective theoretical values.

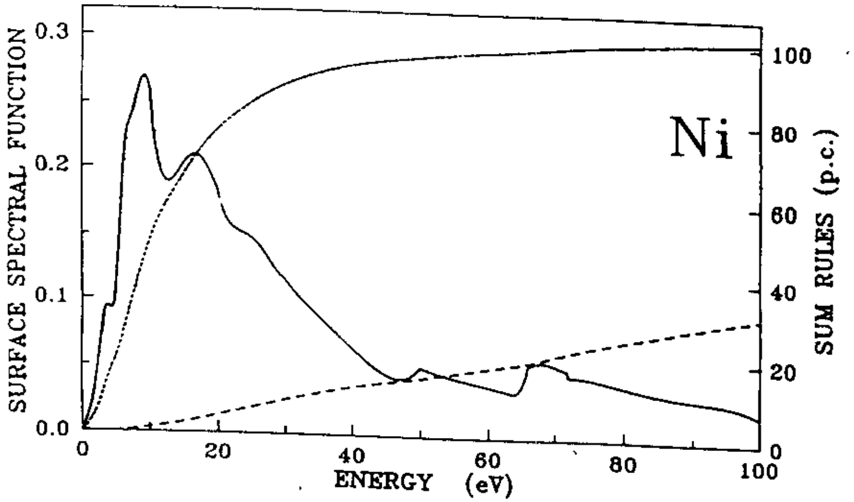


Figure 4.3e: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF NICKEL. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of respective theoretical values.

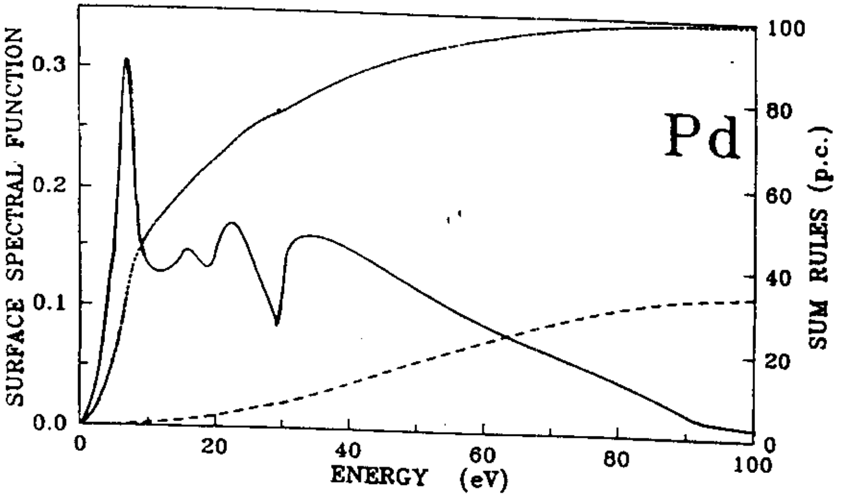


Figure 4.3f: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF PALLADIUM. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of respective theoretical values.

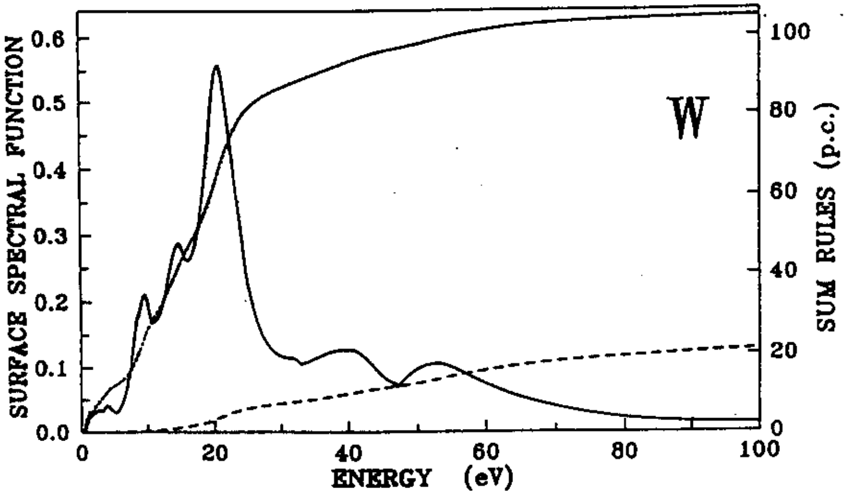
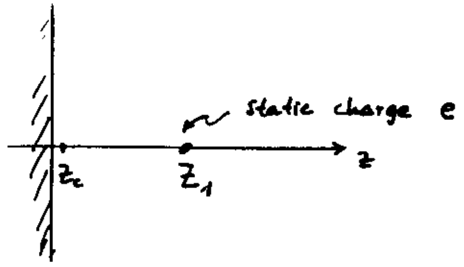


Figure 4.3g: LONG WAVELENGTH SURFACE ELECTRONIC EXCITATIONS SPECTRUM OF TUNGSTEN. Dotted and dashed lines represent the "partial sum rules" (4.19) and (4.20), respectively, plotted in percents of the theoretical values.

C.5. Simple applications

a) Interaction of a static charge with metal surface – image potential



Take a static point charge located at $\vec{r}=(0,0,z_1)$
Then:

$$\varphi_Q(z) = \frac{2\pi e}{Q}\, e^{-Q|z-z_1|} \qquad (\underline{II}.39$$

and for $\omega = 0$

$$R_Q(0) = -(1+2Qz_c). \qquad \Big\{ \text{Follows from perfect screening sum rule}$$

Hence, the image potential (interaction of the charge e with the surface) reads:

$$e\varphi^i(z_1) = \frac{e}{(2\pi)^2}\int \varphi^i_Q(z_1)\, d^2Q = \frac{e}{(2\pi)^2}\int \varphi_Q(-z_1) R_Q(0)\, d^2Q =$$

$$= \frac{e^2}{4(z_1-z_c)}$$

⇒ Classical limit retrieved by the linear response theory! $(\underline{II}.40.)$

b) Surface plasmon dispersion

Using the definition and expression for $R_Q(\omega)$ in the long wavelength limit $Q\to 0$, and the definitions of $d_{\parallel}(\omega)$, $d_\perp(\omega)$ and $d_{\parallel}(\omega)$ we may obtain:

$$\lim_{Q\to 0} R_Q(\omega) = \frac{\omega_s^2[1+Q(d_{\parallel}(\omega)+d_\perp(\omega))]}{\omega^2-\omega_s^2[1+Q(d_{\parallel}(\omega)-d_\perp(\omega))]} \qquad (\underline{II}.41.)$$

$R_Q(\omega)$ will exhibit a pole for <u>complex ω_Q</u> satisfying:

$$\omega_Q^2 - \omega_s^2[1+Q(d_{\parallel}(\omega_Q)-d_\perp(\omega_Q))] = 0.$$

⇒ Thus, surface plasmon dispersion is given by:

$$\omega_Q = \omega_s\left[1+\tfrac{1}{2}Q(d_{\parallel}(\omega_s)-d_\perp(\omega_s))\right] + O(Q^2) \qquad (\underline{II}.42$$

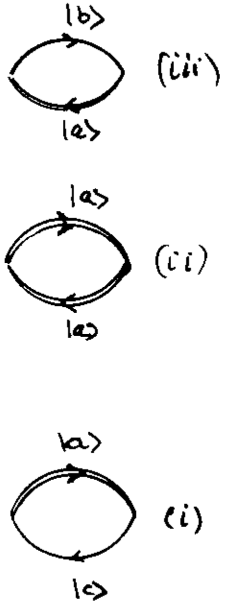
<u>Example:</u>

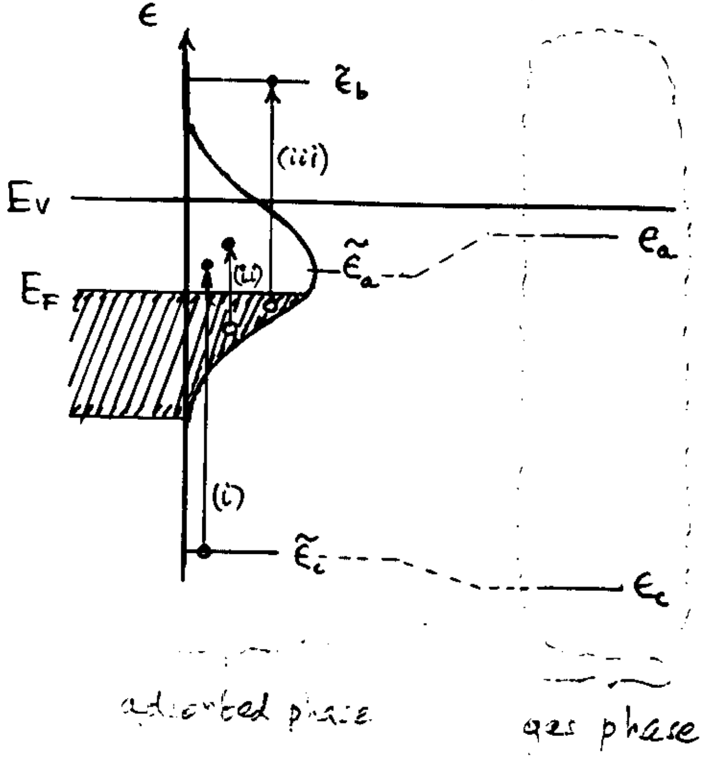
In the simplest approximation using the Ansatz of Zaremba and Kohn (eq. $\underline{II}$.35.) we obtain:

$$\omega_Q^{zk} = \omega_s[1-Q(z_c-z_B)] \,. \qquad (\underline{II}.43.)$$

Dynamic polarizability of chemisorbed adsorbates

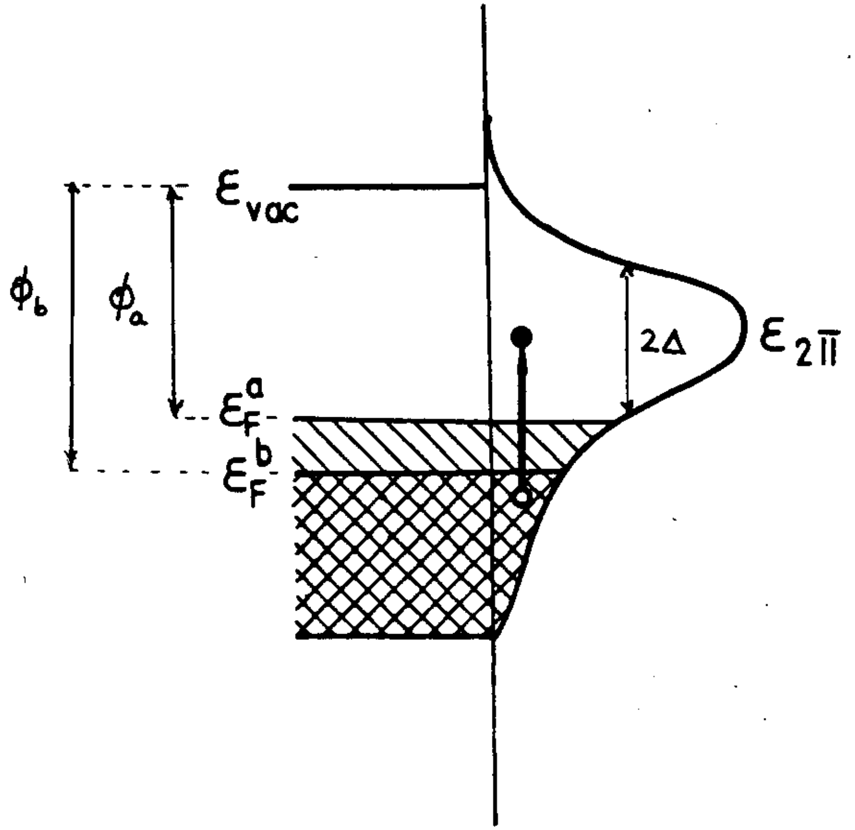
(c.f. Gumhalter & Wandelt PRL 57(1986)2318)





Polarization processes (i), (ii) and (iii) are a consequence of *fractional* occupation of adsorbate valence resonances and, therefore are non existent in gas phase atoms or molecules!

Intra-resonance polarizability $\alpha_{2\pi}(\omega)$
(intra-resonance excitations)



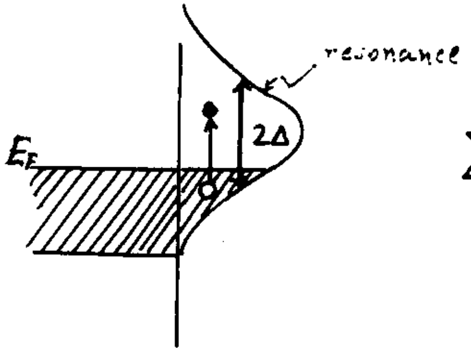
Real. $-\frac{1}{\pi}\,\mathrm{Im}\;R_{2\pi}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}$  $= S_{2\pi}(\omega) = \underbrace{f_{2\pi}(\omega)}$

oscillator strength per unit energy interval

Virt. $\mathrm{Re}\;R_{2\pi}(\omega) = \mathrm{Re}$ 

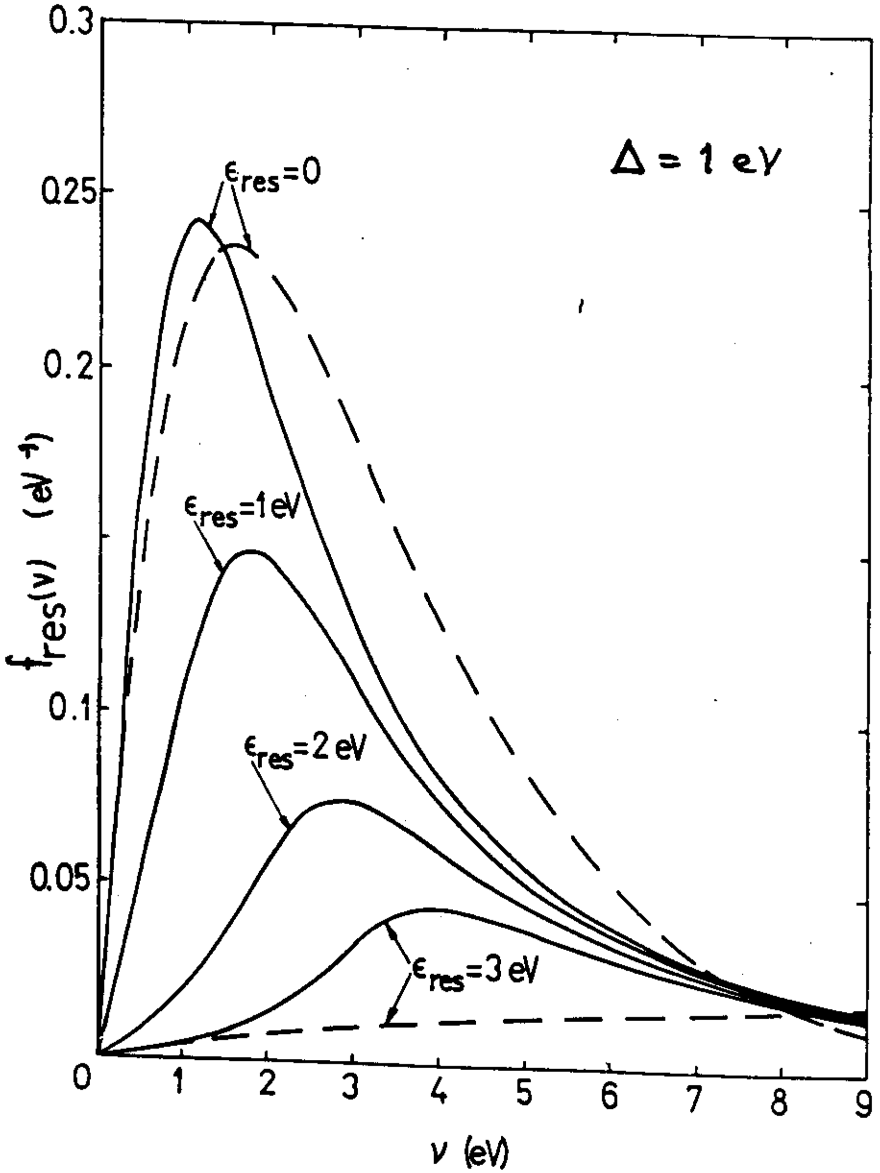
both ϕ dependent! (system specific)

Intra-resonance electronic excitations



$\sum_{i=1}^{g} \bar{n}_i$ .... fractional resonance occupation

g......... resonance degeneracy



Intra-resonance polarizability
(bosonized e-h pairs)

$$\alpha^{res}(\omega) = \int_0^\infty d\omega' \quad \frac{f_{2\pi}(\omega')}{\omega^2 - \omega'^2}$$

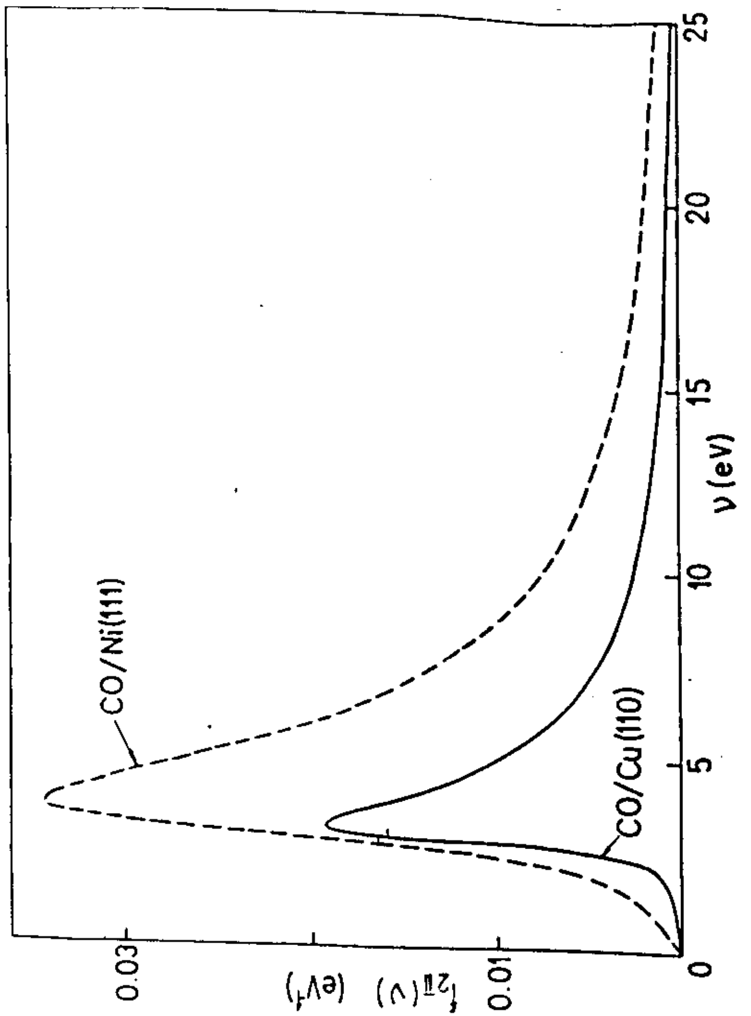
$$\Rightarrow \qquad \mathcal{Z}_{co}(\omega) = \alpha^{d}(\omega) + \alpha^{res}(\omega)$$

Intraresonance f-sum rule in harmonic approx.

$$\int_0^\infty d\omega \quad \underset{\downarrow}{f_{2\pi}(\omega)} \quad = \quad \sum_{i=1}^{g} \quad \bar{n}_i(1-\bar{n}_i) \quad \Big\} \text{ maximum for half occupied resonances!}$$

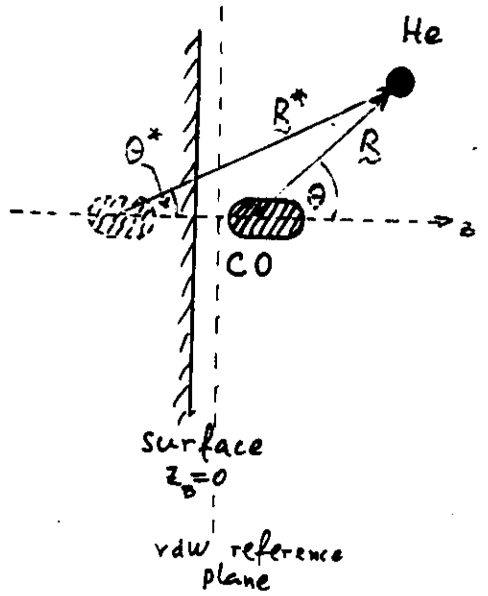
intraresonance
oscillator strength of

$$\alpha_{2\pi}(\omega) = \int_0^\infty d\nu \, \frac{f_{2\pi}(\nu)}{\omega^2-\nu^2}$$ ... intra-resonance polarizabilit

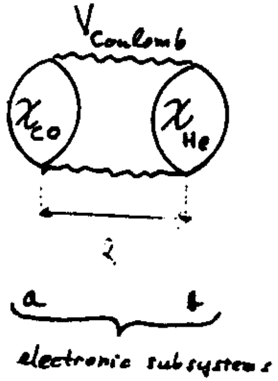


b) Van der Waals potentials for atom - adsorbate scattering

Gumhalter & Liu
Surf. Sci. 148(1984) 371



(i) Gas phase term (direct interaction)



$$V_{dir}(\underset{\sim}{R}) = V_{ab} = -C_1 \frac{C_{ab}}{R^6}\left[1 + \frac{1-\mu}{1+2\mu} P_2(\cos\theta)\right]$$

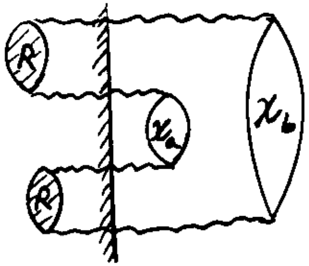
$$C_1 = (2+4\mu) \quad , \qquad \mu = \alpha_{\perp}^{CO}(\omega)/\alpha_0^{CO}(\omega)$$

$$C_{ab} = \int_0^\infty \frac{du}{2\pi} \tilde{\alpha}_a(iu)\,\alpha_b(iu)$$

$\alpha(\omega)$ ... atomic (molecular) polarizability

(ii) Three body surface mediated interactions

Image term



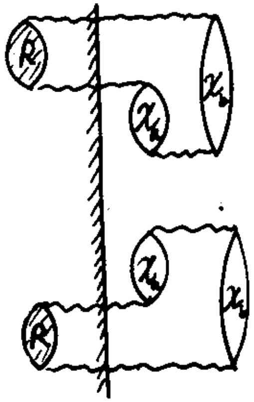
$$V_{im}(\underset{\sim}{R}) = -C_1 \frac{C_{aMbM}}{R^{*6}}\left[1 + \frac{1-\mu}{1+2\mu} P_2(\cos\Theta^*)\right]$$

$$C_{aMbM} = \int_0^\infty \frac{du}{2\pi}\, \tilde{\alpha}_a(iu)\, \alpha_b(iu)\, R_0^2(iu)$$

$\uparrow$

surface response function
in $Q \to 0$ limit

Interference terms



$$V_{int}(\underset{\sim}{R}) = \frac{2C_{abM}}{(R\,R^*)^3}\Big\{(4 - 3\cos^2\Theta - 3\cos^2\Theta^*)$$

$$-(1-\mu)\big[5 + 9\cos^2\Theta\cos^2\Theta^* - 6(\cos^2\Theta + \cos^2\Theta^*)$$

$$+ 9\sin\Theta\sin\Theta^*\cos\Theta\cos\Theta^*\big]\Big\}$$

$$C_{abM} = \int_0^\infty \frac{du}{2\pi}\, \tilde{\alpha}_a(iu)\, \alpha_b(iu)\, R_0(iu)$$

$\Rightarrow$ $V_{dir}(\underset{\sim}{R})$, $V_{im}(\underset{\sim}{R})$ and $V_{int}(\underset{\sim}{R})$ anisotropic !