

## Screening energies in photoelectron spectroscopy of localized electron levels

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Screening or polarization energies (often called "extra-atomic relaxation energies") associated with localized-hole creation in photoelectron spectroscopy in or on metals have been calculated. Following the procedure of Hedin and Lundqvist, the screening energy is written in terms of an effective matrix element of a nonlocal random-phase-approximation self-energy between wave functions of the localized-hole state. The relevance of spatial extent of the hole, electron-gas dielectric properties, chemical-bonding effects, and surface effects are examined. Calculations for  $1s$  core and bonding  $H_2$  orbital holes in atoms or molecules which are embedded in and adsorbed on electron-gas surfaces are presented. The interplay between orbital size and host interelectron spacing (as manifested in screening lengths) is emphasized. The relationship between screening energies and classical image potentials in photoelectron spectroscopy of adsorbed atoms and molecules is established. Finally, interpretations of observed photoelectron spectra are discussed in terms of binding energies and relaxation, chemical, and "dipole" potential shifts, and the problem of "proper" referencing is addressed.

### I. INTRODUCTION

Experimental photoemission spectra from spatially localized electronic levels in solids differ from gas-phase spectra in several important ways. First, the electrostatic potential (relative to the vacuum potential) at the site of the localized state (either core states or impurity-induced virtual states degenerate with the conduction band) is altered due to both the surface dipole barrier and the crystal field from neighboring atoms. This shift in the initial-state energy is often called a chemical shift.<sup>1</sup> It has been hoped that x-ray photoelectron spectroscopy determinations of core-level shifts could easily be used to ascertain some chemical properties of the localized state in the solid-state environment. This hope has been somewhat thwarted due to so-called final-state relaxation effects in which the passive system electrons readjust to the presence of the positively charged hole, lowering their energy by an amount called the relaxation energy.<sup>2-12</sup> Following Shirley,<sup>6</sup> this relaxation energy is often segmented into uncoupled parts: (i) intra-atomic relaxation due to electrons on the atom from which the photoejected electron originated; (ii) extra-atomic relaxation due to polarization or screening by electrons from surrounding atoms. It is then assumed (mostly out of computational necessity) that intra-atomic relaxation remains fixed in going from atomic to solid-state situations, although there are some theoretical suggestions that this may not always be true.<sup>10,13</sup> Neglecting this complication, it then remains to calculate the extra-atomic screening energy in order that chemical information can be extracted from photoelectron spectra.

In particular the present paper treats the problem of screening energies associated with core and non-

bonding valence states of atoms or molecules embedded in and adsorbed on metal surfaces. Both x-ray-photoelectron<sup>14-16</sup> and ultraviolet-photoemission spectroscopy<sup>15-20</sup> experiments have been performed on physisorbed noble gases, chemisorbed atoms and molecules, and condensed molecules on various metal substrates. Attempts have been made to interpret the position of the adsorbate-induced structure in a photoelectron energy distribution in terms of gas-phase spectra modified by some chemical, bonding, and relaxation shifts. However, basic theory underlying such procedures, as applied to adsorption systems, has not yet been worked out in detail. It is the purpose of this paper to advance a theory of the extra-atomic relaxation or screening energy associated with a hole state in an adsorbed atom or molecule. It is already well known that to zero order, this *adsorbate screening energy is just the quantum-mechanical generalization of a classical image potential shift*<sup>12</sup> and this realization marks our point of departure.

A number of alternative approaches for calculating screening energies have appeared.<sup>2-11</sup> Although each theory has its unique set of strengths and weaknesses, most theories seem to obtain roughly equivalent numerical values for localized-hole screening energies, after rather detailed calculations are performed on assumed models (which would be hard to generalize to surface problems). It is this state of affairs which has led to the simple approach adopted in this paper. The basic questions addressed here concern the role of (a) hole spatial extent, (b) metal dielectric properties, (c) chemical-bonding effects, and (d) surface screening on the extra-atomic relaxation energy. Following Hedin *et al.*,<sup>2-4</sup> the screening energy will be expressed as a matrix element of a nonlocal self-energy, evaluated within the elec-

tron-gas random-phase approximation (RPA). Although the model-dependent nature of this approach is its basic weakness, the facts that the numbers it produces are in the same range as the more extensive calculations<sup>9,10</sup> and that the method offers the flexibility of examining systematic trends in questions (a)–(d) give the RPA technique its strengths.

The basic physical input is the realization that the screening charge induced by a localized charge (hole) can be expressed as a coherent sum of virtual bulk or surface-plasmon excitations. The screening energy is just the Coulomb energy between the hole charge distribution and this induced charge. Various aspects of both static and dynamic screening of a point charge by the surface-plasmon field outside a metal (electron-gas) surface have been discussed in recent years and we will draw heavily on this collected wisdom.<sup>21–34</sup> First some confusing ideas concerning plasmon screening should be dispelled. The quantity of interest here is the static screening energy which is related to  $R(\omega)$ , the dynamic density-density response of the system (plasmons) via a Kramers-Kronig transform.<sup>32,36,37</sup> In fact, since the static screening energy is given by<sup>36,37</sup>  $\Delta\epsilon_r \sim \int (d\omega/\omega) \text{Im}R(\omega)$ , knowledge of the excitation spectrum of the solid is required, even though we are dealing with a time-independent ground-state property of the system with a localized hole. There are many intriguing problems related to the time dependence of the relaxation process,<sup>37–43</sup> but in general these problems are concerned with the relative number of ejected electrons in various shakeup satellites compared with the number in the adiabatic threshold peak at an energy corresponding to complete relaxation.<sup>36,37</sup>

The structure of this paper, some of which has already been presented in preliminary form,<sup>12,44</sup> is the following. In Sec. II, the general theory used here for the screening energy of hole states within and outside an electron-gas modeled metal is given. Section III is devoted to localized-hole screening within an infinite electron gas. In particular, the screening of a 1s hole, as a function of hole size, is calculated and the role of spatial extent compared to screening lengths is emphasized. As an exploratory study on the effects of chemical bondings as they relate to screening energies,  $\Delta\epsilon_r$  is calculated for molecular-orbital hole states. Surface screening energies are treated in Sec. IV, where again atomic- and molecular-orbital holes are considered. The possibilities of different values for the screening energy as a function of molecular orientation with respect to the surface (parallel or perpendicular for a diatomic molecule) are explored and a simple image-

like formula is given which takes into account the imperfect screening of a real metal. The effects which have been neglected in the present theory and their anticipated importance along with other loose ends are discussed in Sec. V. The relation between experimental photoemission spectra and the energies calculated here are discussed in Sec. VI. As there has been considerable confusion in the experimental literature on both the problem of reference levels (vacuum level versus Fermi level versus average internal potential) and also nomenclature (some people refer to the sum total of relaxation energy plus chemical shift as a relaxation shift whereas others do not), this situation is also addressed in Sec. VI. Finally, general conclusions are presented in Sec. VII.

## II. POLARIZATION SELF-ENERGY

Within the RPA, the nonlocal polarization self-energy for a quasiparticle with energy  $\epsilon$  is given by<sup>4,28,35</sup>:

$$\Sigma(\vec{r}, \vec{r}'; \epsilon) = \frac{i}{2\pi} \oint d\omega G_0(\vec{r}, \vec{r}'; \epsilon - \omega) \frac{\delta V_{\text{in}}(\vec{r}', \omega)}{\delta n(\vec{r}, \omega)}, \quad (1)$$

where  $\delta V_{\text{in}}(\vec{r}', \omega)/\delta n(\vec{r}, \omega)$  is the  $\omega$ th Fourier component of the potential induced at point  $\vec{r}'$  by a charge at point  $\vec{r}$ .  $G_0$  is the undressed quasiparticle propagator after virtual emission of the density fluctuation, as shown in Fig. 1, for the case of a hole located outside a metal surface. If the hole is localized, then the separation between  $\vec{r}$  and  $\vec{r}'$  is of the order of the hole dimension. The self-energy operator is related to an effective single-particle-like polarization (or relaxation) shift in some hole state  $\phi_a(\vec{r})$  with unrelaxed energy  $\epsilon_a$  by<sup>3,35</sup>:

$$\Delta\epsilon_r = \int d^3r d^3r' \phi_a^*(\vec{r}) \Sigma(\vec{r}, \vec{r}'; \epsilon \approx \epsilon_a) \phi_a(\vec{r}'), \quad (2)$$

which is the basic quantity to be evaluated. Note that the self-energy can be evaluated at the unperturbed energy  $\epsilon_a$  since  $\Sigma$  is a small correction to the strong potential which provided the original

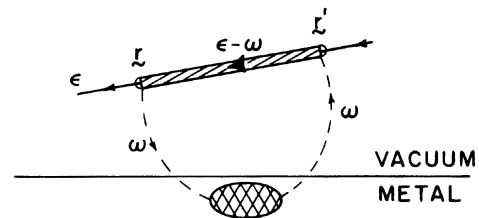


FIG. 1. Hole surface screening self-energy diagram. The hole propagates from  $\vec{r}$  to  $\vec{r}'$  while the virtual density fluctuation is localized within or on the metal.

localization of  $\phi_a$ . This will be discussed further in Sec. V.

The explicit form for the Green's function is

$$G_0(\vec{\mathbf{r}}, \vec{\mathbf{r}}'; \epsilon - \omega) = \sum_x \frac{\phi_x(\vec{\mathbf{r}})\phi_x^*(\vec{\mathbf{r}}')}{\epsilon - \omega - \epsilon_x + i \operatorname{sgn}(\epsilon_x)\delta}, \quad (3)$$

where  $\{\phi_x\}$  is a complete orthonormal set of functions which are solutions of a convenient zero-order problem and  $\epsilon_x$  are the associated one-electron energies, with respect to the Fermi level. In the case of adsorbed objects, the set  $\{\phi_x\}$  is taken to be the atomic or molecular states of the adsorbate only, thus eliminating by ansatz any effects due to itinerant holes.<sup>40,45</sup> (See Sec. V.)

From classical electromagnetism it is fairly straightforward to show<sup>46</sup> that  $\delta V/\delta n$  is given for a hole charge distribution in a uniform (bulk) conductor by

$$\frac{\delta V_{\text{in}}^{\text{D}}(\vec{\mathbf{r}}', \omega)}{\delta n(\vec{\mathbf{r}}, \omega)} = \int \frac{d^3 q}{(2\pi)^3} \left( \frac{1 - \epsilon(q, \omega)}{\epsilon(q, \omega)} \right) \times \left( \frac{4\pi e^2}{q^2} \right) e^{i\vec{q}\cdot(\vec{\mathbf{r}} - \vec{\mathbf{r}}')}, \quad (4)$$

where  $\epsilon(q, \omega)$  is the wave-number and frequency-dependent dielectric function of the medium. Similarly a charge distribution outside a conductor induces a screening charge on the surface which can be related to virtual surface-plasmon excitation<sup>21-35</sup> (or the classical problem of a displaced harmonic oscillator<sup>47</sup>). The corresponding expression for  $\delta V/\delta n$  is

$$\frac{\delta V_{\text{in}}^{\text{D}}(\vec{\mathbf{r}}', \omega)}{\delta n(\vec{\mathbf{r}}, \omega)} = \int \frac{d^2 q}{(2\pi)^2} \left( \frac{1 - \epsilon(q, \omega)}{1 + \epsilon(q, \omega)} \right) \left( \frac{2\pi e^2}{q} \right) \times e^{i\vec{q}\cdot(\vec{\mathbf{r}}_{\parallel} - \vec{\mathbf{r}}'_{\parallel})} e^{-\alpha(|z| + |z'|)}, \quad (5)$$

where now  $\vec{q}$  is a two-dimensional vector parallel to the  $z = 0$  surface.<sup>48</sup>

Expressions for both the bulk and surface screening energies are obtained by combining Eqs. (1)–(4). First, the bulk energy is

$$\Delta\epsilon_r^b = \sum_x \int \frac{d^3 q}{(2\pi)^3} \left( \frac{4\pi e^2}{q^2} \right) \left| \int d^3 r \phi_a^*(\vec{\mathbf{r}})\phi_x(\vec{\mathbf{r}})e^{i\vec{q}\cdot\vec{\mathbf{r}}} \right|^2 \times \frac{i}{2\pi} \int d\omega \left( \frac{1 - \epsilon(q, \omega)}{\epsilon(q, \omega)} \right) \frac{1}{\epsilon_a - \omega - \epsilon_x}. \quad (6)$$

If only the  $x = a$  term is retained in the sum (which is equivalent to assuming a nonpolarizable hole as discussed in Sec. V), then it is possible to retrieve standard results previously obtained for the screening energy of a point charge [ $|\phi_a(\vec{\mathbf{r}})|^2 = \delta^{(3)}(\vec{\mathbf{r}})$ ]. For the remainder of this paper we will work within

this limitation. Defining the three-dimensional Fourier transform of the hole charge density as<sup>49</sup>

$$\rho_{aa}(\vec{\mathbf{q}}) = \int d^3 r |\phi_a(\vec{\mathbf{r}})|^2 e^{i\vec{q}\cdot\vec{\mathbf{r}}}, \quad (7)$$

Eq. (6) then becomes

$$\Delta\epsilon_r^b = \int \frac{d^3 q}{(2\pi)^3} \left( \frac{4\pi e^2}{q^2} \right) |\rho_{aa}(\vec{\mathbf{q}})|^2 \times \frac{1}{2\pi i} \oint \frac{d\omega}{\omega} \left( \frac{1 - \epsilon(q, \omega)}{\epsilon(q, \omega)} \right). \quad (8)$$

From Eqs. (6) and (8) the physical consequence of keeping only the  $x = a$  term has been the decoupling of  $\epsilon(q, \omega)$ , the dynamic response of the electron gas from the dynamic polarizability of the hole, which enters the theory through the location of the pole at  $\omega = \epsilon_a - \epsilon_x$  and whose strength is proportional to  $|\rho_{ax}(\vec{\mathbf{q}})|^2$ . The picture provided by Eq. (8) is one in which a rigid hole, with a spatial extent determined by  $\rho_{aa}(\vec{\mathbf{q}})$ , is statically screened by the electron gas. Mathematically this follows from Eq. (8) since  $1/2\pi i$  times the integral on  $\omega$  is just the Kramers-Kronig transform relating the static and dynamic dielectric responses.<sup>32</sup> Equation (8) reduces to

$$\Delta\epsilon_r^b \simeq \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} \left( \frac{4\pi e^2}{q^2} \right) \left( \frac{1 - \epsilon(q, 0)}{\epsilon(q, 0)} \right) |\rho_{aa}(\vec{\mathbf{q}})|^2, \quad (9)$$

which is the expression previously obtained in a much different way.<sup>12,44</sup> The advantages of the present approach are that we have been able to pinpoint the microscopic level approximations implicit in the screening-energy expression and to provide a quantitative means for improving upon them [Eq. (6)].

Proceeding in an analogous manner for the case in which the hole is on an adsorbate, outside the surface, Eqs. (1)–(3) and (5) yield

$$\Delta\epsilon_r^s = \int \frac{d^2 q}{(2\pi)^2} \left( \frac{2\pi e^2}{q} \right) \left| \int_{-\infty}^{\infty} dz e^{-\alpha|z|} \rho_{aa}(\vec{\mathbf{q}}, z) \right|^2 \times \frac{1}{2\pi i} \oint \frac{d\omega}{\omega} \left( \frac{1 - \epsilon(q, \omega)}{1 + \epsilon(q, \omega)} \right), \quad (10)$$

where the two-dimensional Fourier transform of the hole charge density is defined by

$$\rho_{aa}(\vec{\mathbf{q}}, z) \equiv \int d^2 r_{\parallel} |\phi_a(\vec{\mathbf{r}}_{\parallel}, z)|^2 e^{i\vec{q}\cdot\vec{\mathbf{r}}_{\parallel}}. \quad (11)$$

As with Eqs. (8) and (9), the retention of the  $x = a$  term only wipes out the coupling between the  $\omega$  dependence of  $\epsilon$  and the  $q$  dependence of  $\rho_{aa}(\vec{\mathbf{q}}, z)$ . As discussed in Sec. V, this coupling would give rise to an effective van der Waals-type energy,

mathematically expressed in the form of a Lifshitz-like equation.<sup>50</sup> Performing the Kramers-Kronig transform in Eq. (10),

$$\Delta\epsilon_r^s = \frac{1}{2} \int \frac{d^2q}{(2\pi)^2} \left( \frac{2\pi e^2}{q} \right) \left( \frac{1 - \epsilon(q, 0)}{1 + \epsilon(q, 0)} \right) \times \left| \int_{-\infty}^{\infty} dz e^{-q|z|} |\rho_{aa}(\vec{q}, z)|^2 \right. \quad (12)$$

Equations (9) and (12) are the basic equations, upon which all calculations in this paper will be based.

### III. BULK SCREENING ENERGY

In order to gain some insight into the relationship between hole size, dielectric screening properties, chemical bonding, and screening energies, it is informative to look first at the cases in which an atom or molecule are embedded in a homogeneous electron gas and in subsequent sections worry about the extra complications due to surface effects.

#### A. Atoms or core states

If we consider a spherically symmetric hole, the angular integration in Eq. (9) is trivial yielding

$$\Delta\epsilon_r^b = \frac{e^2}{\pi} \int_0^{\infty} dq \left( \frac{1 - \epsilon(q, 0)}{\epsilon(q, 0)} \right) |\rho_{aa}(q)|^2, \quad (13)$$

which with a Fermi-Thomas dielectric function  $\epsilon(q, 0) = 1 + \kappa^2/q^2$  is

$$\Delta\epsilon_r^b = \frac{e^2 \kappa^2}{\pi} \int_0^{\infty} dq \frac{|\rho_{aa}(q)|^2}{q^2 + \kappa^2}, \quad (14)$$

where  $\kappa = 2.95/r_s^{1/2} \text{ \AA}^{-1}$  is the inverse screening length. For a  $\delta$ -function hole charge density  $\rho_{aa}(\vec{r}) = \delta^{(3)}(\vec{r})$ ,  $\rho_{aa}(\vec{q}) = 1$  for all  $q$  and Eq. (14) is straightforwardly  $\Delta\epsilon_r^b(\text{point}) = e^2 \kappa/2$ .

Next consider a hole in a  $1s$  state in which the hydrogenic function is approximated by a single optimum Gaussian wave function<sup>51</sup>

$$\phi_{1s}(\vec{r}) = \left( \frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2},$$

with  $\alpha = 0.96 \text{ \AA}^{-2}$ . The hole charge-density Fourier components associated with this state are<sup>52(a)</sup>

$$\rho_{1s}(q) = \int d^3r e^{i\vec{q}\cdot\vec{r}} |\phi_{1s}(\vec{r})|^2 = e^{-q^2/8\alpha}. \quad (15)$$

Consequently, in the Fermi-Thomas approximation, the relaxation energy obtained from Eqs. (14) and (15) is

$$\begin{aligned} \Delta\epsilon_r^b(\text{atom}) &= \frac{e^2 \kappa^2}{\pi} \int_0^{\infty} \frac{dq e^{-q^2/4\alpha}}{q^2 + \kappa^2} \\ &= \frac{e^2 \kappa}{2} e^{\kappa^2/4\alpha} [1 - \text{erf}(\kappa/2\alpha^{1/2})]. \end{aligned} \quad (16)$$

For the Gaussian orbital,  $\alpha$  is related to the mean radius as  $\langle r \rangle = (2/\pi\alpha)^{1/2}$ . From Eq. (16),  $\Delta\epsilon_r^b$  (atom) as a function of  $\langle r \rangle$  has been calculated treating  $r_s$  parametrically and the results are given in Fig. 2. As expected, the relaxation energy is reduced significantly when the spatial extent of the hole charge density is comparable to or greater than  $\sim 1/\kappa$  (marked by the vertical line). The physical origin of this reduction is clearly illustrated through Eq. (16). The screening of the hole is due to a coherent superposition of electron-gas density fluctuations with wave numbers  $q$ . To achieve the perfect localization of a point hole, Fourier components of all wave numbers are required, hence  $\rho_n(q) = 1$  for all  $q$ , and the entire density-fluctuation spectrum contributes to the screening charge and thus energy. On the other hand, for a spatially extended hole, few Fourier components with  $q \gtrsim 1/\langle r \rangle$  are required to localize the hole and thus the contribution to the screening energy from short-wavelength density fluctuations ( $\lambda \ll \langle r \rangle$ ) is small. From Eq. (16) it is apparent that if the spatial extent of the hole (as manifest in the Gaussian) is such that  $1/\langle r \rangle \approx q_{\text{max}}$  is much less than the inverse screening length  $\kappa$ , then the integral will be reduced from the  $q_{\text{max}} = \infty$  point-hole limit. However, if  $q_{\text{max}} \gg \kappa$ , the denominator, which expresses the properties of the electron-gas density fluctuations, will cut off the integral in a way which is rather insensitive to the value of  $\langle r \rangle$ . For values of  $r_s$  in the real metal range ( $2 \lesssim r_s \lesssim 5$ ),  $1/\kappa \gg \langle r_{\text{core}} \rangle \sim 0.1 \text{ \AA}$ , and thus the screening energy should not vary appreciably due to varying electron-gas properties. Lastly note that the absolute values of these numbers are

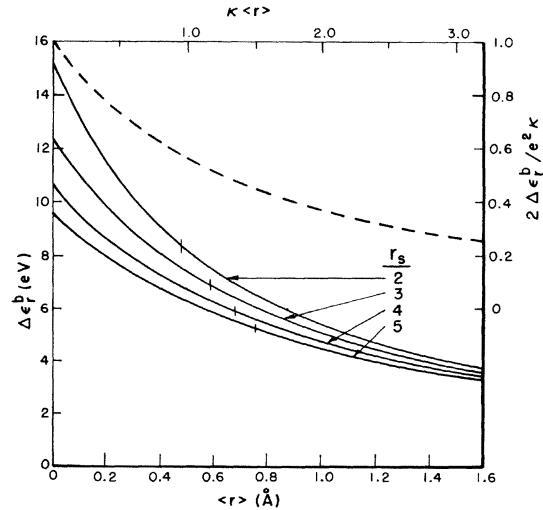


FIG. 2. Bulk screening energy versus hole radius with parametric  $r_s$  depicted by the full curves and left-hand and bottom axis. Nondimensionalized form is shown as the dashed curve with right-hand and top axis.

roughly a factor of two larger than the screening energies calculated for implanted rare-gas impurities in noble-metal hosts.<sup>9,10</sup> In part, this is due to an oversimplification in the electron-gas theory (which, however, is of minimal importance in the adsorbate case).<sup>52(b)</sup> As pointed out by Citrin and Hamann<sup>9</sup> and Watson, Herbst, and Wilkins,<sup>10</sup> the wave functions of the screening electrons must be orthogonal to the core electrons. In pseudopotential language, this is accounted for by introducing a repulsive pseudopotential which pushes the screening charge out from the region of the core hole. Consequently the screening energy is lowered compared to electron-gas results where screening charge is allowed to pile up nearer to the core hole. For this reason, the absolute numbers for  $\Delta\epsilon_r$  in Fig. 2 are unrealistically large. On the other hand, in the ratio  $2\epsilon_r^b(\text{atom})/e^2\kappa$ , also shown in Fig. 2, the neglect of orthogonalization errors approximately cancel and physical conclusions derived from this curve are more realistic.

### B. Molecules

If two atoms interact to form a simple chemical bond, then, at least in a molecular-orbital (MO) picture, the electrons originally occupying the constituent atomic orbitals, delocalize into the spatially more extended MOs. Since the screening energy is inversely proportional to the volume of the localized-hole state, it is essential to know how the screening energy changes, upon bond formation and thus hole delocalization, if photoemission spectroscopy is to be used as a quantitative technique for chemisorption studies involving bonding orbitals.

As a first step in understanding this relaxation effect, consider the simplest possible case, that of a diatomic  $H_2$  molecule embedded in an electron gas. Upon photoejection, a hole is created in an MO state

$$\psi(\vec{r}) = N [\phi_{1s}(\vec{r} - \vec{R}_a) + \phi_{1s}(\vec{r} - \vec{R}_b)],$$

where  $\phi(a)$  or  $\phi(b)$  are  $1s$  atomic orbitals on each center at  $\vec{R}_a$  or  $\vec{R}_b$  with  $|\vec{R}_a - \vec{R}_b| \equiv s$  and the normalization constant  $N = 1/\sqrt{2(1+S)^{1/2}}$  with  $S = \langle a|b \rangle$  the overlap integral. The hole charge density is then

$$\rho_{aa}(\vec{r}) = N^2 [ |\phi_{1s}(\vec{r} - \vec{R}_a)|^2 + |\phi_{1s}(\vec{r} - \vec{R}_b)|^2 + 2\phi_{1s}(\vec{r} - \vec{R}_a)\phi_{1s}(\vec{r} - \vec{R}_b) ]. \quad (17)$$

The first two terms on the right-hand side of Eq. (17) are atomic-charge distributions on each of

the two centers, but with total occupation  $< \frac{1}{2}$  per center. The remaining charge, given by the constructive interference term, is called the quantum-mechanical bonding charge and is concentrated between the two centers.

In dealing with multicenter molecular problems it is convenient to write the atomic orbitals as an expansion in Gaussians:

$$\phi_{1s}(r) = \sum_{k=1}^N d_k \left( \frac{2\alpha_k}{\pi} \right)^{3/4} e^{-\alpha_k r^2}.$$

We will use the coefficients  $d_k$  and exponents  $\alpha_k$  suggested by Stewart<sup>51</sup> for  $N = 4$ . The desirable feature of the Gaussian expansion is that the two center bonding charge density in Eq. (17) is given by a sum of Gaussians<sup>52</sup> and Fourier transformation is thus straightforward. With  $\vec{R}_a = \mp \frac{1}{2}s\hat{z}$  (since the infinite electron gas is translationally and rotationally invariant), the Fourier transforms of the atomic-charge densities in Eq. (17), with respect to an origin midway between  $a$  and  $b$  are

$$\begin{aligned} \rho_{a,b}(\vec{q}) &= \int d^3r e^{i\vec{q}\cdot\vec{r}} |\phi_{1s}(\vec{r} \pm \frac{1}{2}s\hat{z})|^2 \\ &= e^{\pm i q_z s/2} \rho_0(q), \end{aligned} \quad (18)$$

with

$$\begin{aligned} \rho_0(q) &= \sum_{k=1}^N \sum_{l=1}^N d_k d_l \left( \frac{2(\alpha_k \alpha_l)^{1/2}}{\alpha_k + \alpha_l} \right)^{3/2} \\ &\quad \times \exp[-q^2/4(\alpha_k + \alpha_l)]. \end{aligned} \quad (19)$$

Consequently,

$$\rho_a(\vec{q}) + \rho_b(\vec{q}) = 2 \cos(\frac{1}{2}q_z s) \rho_0(q). \quad (20)$$

Following standard procedure,<sup>52</sup> the Fourier transform of the bonding charge can be written

$$\begin{aligned} \rho_{bc}(\vec{q}) &= \int d^3r e^{i\vec{q}\cdot\vec{r}} \phi_{1s}(\vec{r} - \frac{1}{2}s\hat{z}) \phi_{1s}(\vec{r} + \frac{1}{2}s\hat{z}) \\ &= \sum_{k=1}^N \sum_{l=1}^N d_k d_l \left( \frac{2(\alpha_k \alpha_l)^{1/2}}{\alpha_k + \alpha_l} \right)^{3/2} \\ &\quad \times \exp[-\alpha_k \alpha_l s^2 / (\alpha_k + \alpha_l)] \\ &\quad \times \exp[-q^2/4(\alpha_k + \alpha_l)]. \end{aligned} \quad (21)$$

Combining Eqs. (17)–(21), the  $q$ th Fourier component of the hole charge density is

$$\rho_{aa}(\vec{q}) = 2N^2 [\rho_0(q) \cos(\frac{1}{2}q_s \cos\theta) + \rho_{bc}(q)] \quad (22)$$

with  $q_z = q \cos\theta$ . Inserting Eq. (22) in Eq. (9) and performing the angular integrations yields, for the screening energy,

$$\Delta\epsilon_r^b = \frac{e^2}{2\pi(1+S)^2} \int_0^\infty dq \left( \frac{1 - \epsilon(q, 0)}{\epsilon(q, 0)} \right) \left[ \rho_0(q)^2 \left( 1 + \frac{\sin qs}{qs} \right) + 2\rho_{bc}(q)^2 + 4\rho_0(q)\rho_{bc}(q) \frac{\sin(qs/2)}{qs/2} \right]. \quad (23)$$

Equations (18), (21), and (23) have been evaluated numerically as a function of  $\kappa s$ , using both the Fermi-Thomas and RPA (random-phase-approximation) dielectric functions and treating  $r_s$  parametrically. The results are shown in Fig. 3. The internuclear separation for  $H_2$  and  $H_2^+$  in the gas phase ranges from 0.74 to 1.06 Å and this span of  $s$  values is marked by the vertical lines in Fig. 3.

Within the MO framework, these results have the following meaning: As  $s \rightarrow 0$ ,  $\rho_{bc}(q) = \rho_0(q)$  by comparing Eqs. (19) and (21),  $S = 1$ , and Eq. (23), the molecular screening energy, goes precisely to Eq. (13), the atomic value. As the atomic orbital is stretched out into an MO (the consequence of increasing  $s$  from zero), the volume of the single electron orbital increases and thus one would intuitively expect the screening energy for the bonding MO to be reduced. The percentage decrease in  $\Delta\epsilon_r$  (molecule) compared to  $\Delta\epsilon_r$  (atom) (for  $s$  in the  $H_2$  to  $H_2^+$  range) is shown in the insert in Fig. 3 to be always less than 10% for real metal values of  $r_s$ . At least in the case of  $H_2$ , it appears that approximating the  $H_2$  screening energy by the H energy is not too bad, and thus the extra delocalization due to bond formation is not quantitatively very important. However, due to the small size of both H and  $H_2$ , comparable with  $1/\kappa$ , this approximation may not be as valid for larger molecules.

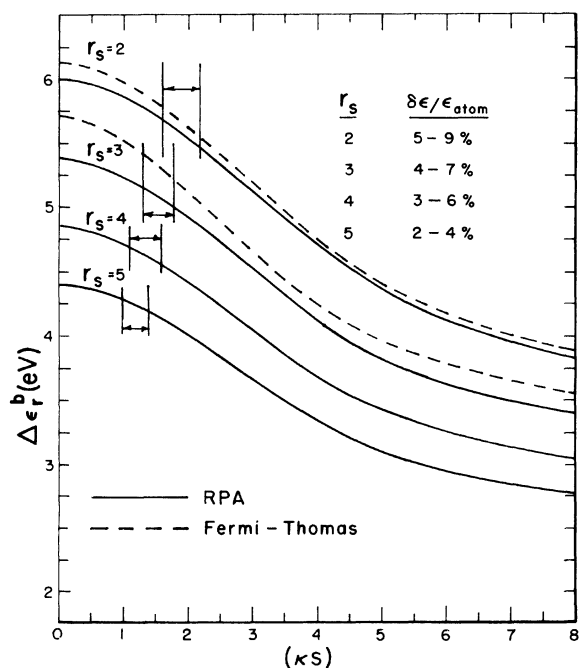


FIG. 3. Bulk screening energy versus  $\kappa s$  for an implanted  $H_2$  molecule, treating  $r_s$  parametrically. The solid curves are the values with an RPA dielectric function and the dashed curves with a Fermi-Thomas one.

In the other extreme limit  $s \rightarrow \infty$ , the MO picture suggests two protons with "one-half a hole" on each center. The screening energy goes as the square of the hole charge  $\sim \frac{1}{4}$  but there are two of these holes so the energy is down by  $\frac{2}{4}$  compared to the atomic value. This is obviously an unphysical result which stems from the lack of correlations in the MO theory. As the internuclear separation increases, correlation effects which are the major ingredient of a pure Heitler-London theory, require the hole to be on one or the other proton with the other partner a H atom, and in this picture  $\Delta\epsilon_r$  returns to the correct atomic value for large  $s$ . Fortunately in the range of applicable  $s$  values for ground-state  $H_2$ , the simple uncorrelated MO theory is reasonable for present purposes. In the Heitler-London model, the hole is itinerant, hopping back and forth between the two centers. The hole hopping time scale is set by the bonding-antibonding orbital-energy separation,  $2V$ ; i.e.,  $\tau_{\text{hopping}} \sim \hbar/2V$ . If this time is long compared with some characteristic screening time  $\tau_{sc}$  usually assumed to be of the order of the inverse plasmon frequency,<sup>53</sup> then the screening charge is able to slavishly follow the instantaneous position of the hole and the resulting screening energy is that one associated with a single atomic orbital. In our case, as  $s \rightarrow \infty$ ,  $V \rightarrow 0$  and thus  $\tau_{\text{hopping}} \gg \tau_{sc}$  so the atomic limit is retrieved. On the other hand when  $\tau_{\text{hopping}} \approx \tau_{sc}$ , the screening charge cannot respond swiftly enough to the instantaneous hole position and thus sees a time-averaged hole distribution which is the delocalized MO distribution treated here. This effect has been discussed by Doniach<sup>40</sup> and then Hewson and Newns<sup>31</sup> in slightly different contexts and more recently by Schrieffer<sup>45</sup> with regards to photoemission spectroscopy of surfaces.

#### IV. SURFACE SCREENING ENERGY

The major thrust of this paper concerns the screening or extra-atomic relaxation energies of hole states that are localized on adsorbates outside the metal surface. In the limit in which either the hole size is small or the hole-surface separation is large compared to a characteristic screening length of the metal, the screening energy is expected to go over to a classical image potential shift.<sup>12</sup> It is our purpose to see how such considerations as finite orbital size, hole-surface separation, molecular orientation, and finite screening properties alter the classical image result. First we will investigate the surface screening response to a 1s hole which could be in a H valence state. An experimentally more relevant and realistic system is a 1s core hole in say

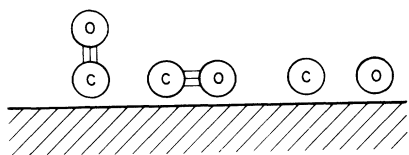


FIG. 4. Some reasonable CO adsorption geometries.

C or O, either atomically or molecularly adsorbed. In fact CO adsorption on various transition metals constitute some of the most widely studied systems<sup>54</sup> using photoemission and even still there is no universal agreement on such fundamental questions as to the state of CO dissociation on the surface.<sup>15(b)</sup> As Brundle has emphasized,<sup>15</sup> doing core-level XPS in conjunction with valence-level UPS is a much more powerful tool than one without the other. Presumably relative 1s core-level shifts in the C and O vary in the different steric configurations shown in Fig. 4. Thus observation of the changes in screening energy might even be a useful diagnostic aid rather than a hinderance, if meaningful theoretical predictions for 1s core shifts are available.

#### A. Atoms or core states

First consider the case of perfect screening. Microscopically this implies infinite free-electron density or  $r_s \rightarrow 0$ ,  $\kappa \rightarrow \infty$ , and thus  $(1 - \epsilon)/(1 + \epsilon) \rightarrow -1$  in Eq. (12), yielding

$$\Delta \epsilon_r^s = -\frac{e^2}{4\pi} \int_0^{q_{up}} dq \int_0^{2\pi} d\phi \left| \int_{-\infty}^{\infty} dz e^{-q|z|} \rho_{aa}(\vec{q}, z) \right|^2, \quad (24)$$

where now an upper cutoff to the  $q$  integral has been inserted. Some important and controversial physics is implied by this inclusion<sup>55</sup> (which will be inconsequential to the results reported here). This will be discussed shortly.

The simplest hole charge distribution is that of a point charge, a distance  $s$  from the surface. With  $\rho_{aa}(\vec{r}) = \delta^{(2)}(\vec{r}_{\parallel}) \delta(z - s)$ ,  $\rho_{aa}(\vec{q}, z) = \delta(z - s)$  and Eq. (24) integrates to

$$\Delta \epsilon_r^s = \frac{e^2}{4s} (1 - e^{-2q_{up}s}), \quad (25)$$

which in the limit  $q_{up}$  or  $s \rightarrow$  large is just the classical image shift. Equation (24) has been obtained previously by Feibelman *et al.*<sup>28</sup> and in the context of surface relaxation energies by Laramore and Camp.<sup>33</sup> Various proposals for picking the value of  $q_{up}$  have been suggested.<sup>55</sup> These include Fermi and Fermi-Thomas wave numbers, the value of  $q$  for which the plasmon dispersion curve hits the electron-hole pair continuum,  $1/\sqrt{2}$  times this value, and the inverse electron-electron separa-

tion. Needless to say, any theoretical result which depends sensitively on the numerical value of such an ill-defined quantity as  $q_{up}$  must be viewed with caution. In fact the controversy just mentioned<sup>55</sup> centers around a theory of surface energies whose end numbers are a strong function of  $q_{up}$ .

The physical significance (and irrelevance here) of the cutoff can easily be seen through Fig. 5. Here a spatially extended hole centered a distance  $s$  from the surface induces a screening charge which can be expressed as a superposition of surface charge-density fluctuations or in other words surface plasmons. Shown in Fig. 5 are two limiting cases in which the surface-plasmon wavelength is much smaller ( $\lambda_s$ ) or larger ( $\lambda_l$ ) than either the hole size or distance from the surface. If  $r_h < s$  and  $\lambda_s \ll s$  then the Coulomb interaction between the  $\lambda_s$  (large  $q$ ) surface-plasmon field and the hole will average to zero and the screening energy will be independent of  $q_{up}$ . This is clear from Eq. (25) also. For a spatially extended hole, it is physically apparent from Fig. 5 that the significant hole-surface plasmon interactions occur near  $\lambda_l$  and approach zero when  $\lambda_s \ll r_h$ . Mathematically  $\rho_{aa}(\vec{q}, z)$  in Eq. (24) cuts off the  $q$  integral when  $q$  exceeds  $1/r_h$ , even if  $s$  is small so again the need to avoid divergences by assigning a value to  $q_{up}$  is averted. Laramore and Camp<sup>32</sup> also calculated the bulk plasmon screening energy and, counter-intuitively, found this to be smaller than the surface screening energy leading then to conclude that "the core hole is more effectively screened at the surface than in the bulk," in agreement with the preliminary interpretation of some experimental results of Houston, Park, and Laramore.<sup>56</sup> These conclusions can be questioned on a number of grounds. Four points bear on the present discussion. First, the Laramore and Camp surface screening energies depend strongly on the well-guided but still arbitrary assignment of a value for  $q_{up}$ . Second, a reasonable prescription for relating the  $z = 0$  plane

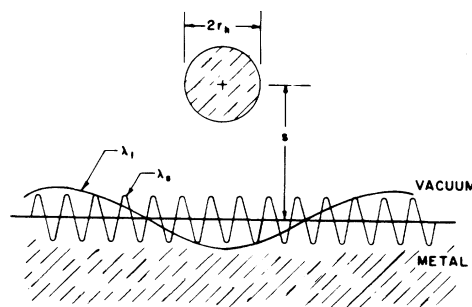


FIG. 5. Schematic diagram illustrating the various relevant distances for screening of an adsorbate hole of radius  $r_h$  a distance  $s$  from the screening plane. Surface plasmons of various limiting wavelengths are shown as the sine waves.

in the electron gas to the location of the effective screening plane in a real metal, relative to the ion cores, must be given before comparison between experiment and theory can be made. Such a prescription was not given by Laramore and Camp, thus leaving the value of  $s$  as yet another fitting parameter. A well-defined procedure (although somewhat arbitrary) will be given in Sec. V. Third, as pointed out by Chang and Langreth<sup>26</sup> who performed similar calculations, significant Friedel-like oscillations in the point-charge screening energy occur, as a function of distance into the surface. These oscillations produce local maxima in the energy which at times exceed the bulk value. In the context of the presently discussed theories, Chang and Langreth suggest that these maxima are mathematical artifacts due to sharp integral truncation and have nothing to do with more efficient screening in the surface region. Lastly, the basic structure of the surface-plasmon screening model may give rise to anomalously large screening energies for point holes located in the  $z = 0$  plane. By construction, an external charge induces a surface screening charge constrained to a layer of zero thickness at  $z = 0$ . In a real system, the screening charge can spread out to a certain degree in the normal direction. Thus the surface-plasmon model probably overestimates the surface screening when the hole is right at the surface as the induced charge is forced, by imposed boundary conditions, to pile up closer to the hole than it would in a real system. For this reason, our considerations are restricted to holes outside the surface.

Moving on to the spatially extended 1s hole outside the surface, the two-dimensional Fourier transform of the 1s Gaussian charge density is

$$\rho_{aa}(\vec{q}, z) = (2\alpha/\pi)^{1/2} e^{-2\alpha(z-s)^2} e^{-q^2/8\alpha}, \quad (26)$$

where now the  $z$  origin is shifted from the core center to the surface. Inserting Eq. (26) in Eq. (24) and noting that all the  $z$  integrals can be cast into the form<sup>57</sup>

$$\int_0^\infty e^{-z^2/4\beta - \gamma z} dz = (\pi\beta)^{1/2} e^{\beta\gamma^2} [1 - \Phi(\gamma\sqrt{\beta})],$$

where  $1 - \Phi$  is the error function, the perfect conductor ( $q_{up} = \infty$ ) screening energy, Eq. (24), is

$$\Delta\epsilon_r^s = \frac{e^2}{8} \int_0^\infty dq \left\{ e^{-qs} \left[ 1 - \Phi\left(\frac{q-4\alpha s}{\sqrt{8\alpha}}\right) \right] + e^{+qs} \left[ 1 - \Phi\left(\frac{q+4\alpha s}{\sqrt{8\alpha}}\right) \right] \right\}. \quad (27)$$

Equation (27) has been evaluated numerically as a function of  $s$  treating  $\alpha$  and thus  $\langle r \rangle$  parametrically. The ratio of  $\Delta\epsilon_r^s$  to the point-charge image

energy  $e^2/4s$  versus  $s$  is shown in Fig. 6. These results can be regarded as an adequate first approximation to the screening energy if  $s > \langle r \rangle$ . Note though that in all cases,  $R \equiv \Delta\epsilon_r^s/\epsilon_{im} \approx 0.9$ , rapidly approaching unity when this condition is fulfilled. Upon reflection, this is not surprising since Eq. (27) is derived from a model which must reduce to the perfect image potential if the hole charge distribution is totally outside the surface. In addition, if the charge distribution is symmetric about  $z = s$ , then the screening energy does not depend on the distribution in the transverse direction, for a perfect conductor surface, if  $\langle r \rangle < s$ .

Finite screening effects can be included in a number of ways. The simplest is to impose a finite  $q_{up}$  in Eq. (24), as has been discussed. Another way is to include plasmon dispersion. Lundqvist<sup>58(a)</sup> and later Overhauser<sup>58(b)</sup> have worked with the so-called plasmon pole dielectric function

$$\epsilon(q, \omega) = 1 - \omega_p^2/(\omega^2 - c^2 q^2) \quad (28)$$

in which  $c$  is some number obtained from the plasmon dispersion relation and  $\omega_p$  is the  $q = 0$  plasmon frequency. Equation (28) can be inserted in Eq. (10) and the  $\omega$  integral performed. Again it is just the  $\omega = 0$  part of  $\epsilon(q, \omega)$  which is required. Note that from Eq. (28),  $\epsilon(q, 0) = 1 + \omega_p^2/c^2 q^2$ . In fact,  $c$  is such that  $\omega_p/c = \kappa$  and thus the Fermi-Thomas dielectric function results from the transformed dynamic  $\epsilon$  which includes plasmon dispersion.<sup>4, 57, 58</sup> The factor  $(1 - \epsilon)/(1 + \epsilon)$  in Eq. (12) is just  $(1 + 2q^2/\kappa^2)^{-1}$  which is a Lorentzian with half-width at half-maximum  $= \kappa/\sqrt{2}$ . For a spherical hole, the screening energy from Eq. (12) is then

$$\Delta\epsilon_r^s = \frac{e^2}{2} \int_0^\infty dq \frac{1}{1 + 2q^2/\kappa^2} \left| \int_{-\infty}^\infty dz e^{-q|z|} \rho_{aa}(\vec{q}, z) \right|^2 \quad (29)$$

which is the surface analog to Eq. (14), the bulk screening energy. The same interpretation of hole

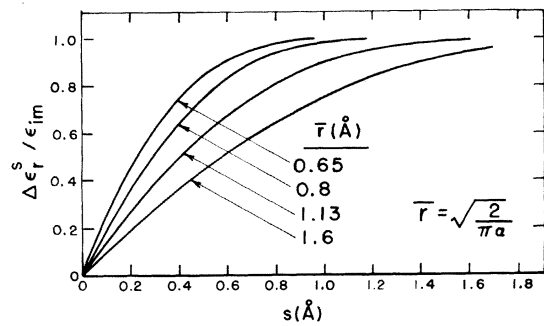


FIG. 6. Ratio of extended 1s hole screening energy over the point-charge image potential versus distance from surface for a perfect conductor. The hole radius is treated parametrically.

size, manifested in  $\rho_{aa}(\vec{q}, z)$ , versus screening length as was given after Eq. (14) applies here. With a 1s orbital,  $\rho_{aa}(\vec{q}, z)$  is given by Eq. (26), which when inserted in Eq. (29) gives the ratio

$$R \equiv \Delta\epsilon_r^s / \epsilon_{im} = \frac{s}{2} \int_0^\infty dq \frac{1}{1+2q^2/\kappa^2} \left\{ e^{-qs} \left[ 1 - \Phi \left( \frac{q-4\alpha s}{(8\alpha)^{1/2}} \right) \right] + e^{+qs} \left[ 1 - \Phi \left( \frac{q+4\alpha s}{(8\alpha)^{1/2}} \right) \right] \right\}^2. \quad (30)$$

Equation (30) is plotted in Fig. 7 as a function of  $s$ , treating  $r_s$  parametrically (with  $\alpha = 0.96 \text{ \AA}^{-2}$ ). For "reasonable" values of  $\alpha$  corresponding to hole radii  $\langle r \rangle \lesssim 0.6 \text{ \AA}$ , the variations in  $R$  as a function of  $\alpha$  or  $\langle r \rangle$ , for given  $s$ , were not significant, provided  $s > \langle r \rangle$ . This follows from the fact that the screening function  $(1+2q^2/\kappa^2)^{-1}$  cuts off the  $q$  integrand before the truncation due to hole extension is felt. However if  $\langle r \rangle \gtrsim \sqrt{2}/\kappa$  (which it never is for 1s states and metallic densities), then  $\Delta\epsilon_r^s$  decreases and in the limit in which  $\langle r \rangle \rightarrow \infty$ ,  $\Delta\epsilon_r^s \rightarrow 0$ . From Fig. 7, it can be seen that the finite screening effect substantially lowers the value of  $\Delta\epsilon_r^s$ , to about 80% of the perfect-screening result for atomic scale hole-surface separations ( $s \approx 1 \text{ \AA}$ ). Long ago the expression  $V_{im} \approx e^2/4(s+\kappa^{-1})$  was suggested<sup>59</sup> for the classical image potential corrected for imperfect screening. For  $s \sim 1 \text{ \AA}$ ,  $V_{im}$  is reduced to  $\sim 70\%$  of the classical result, which is in accord with the numbers of Fig. 7. These are the ones to use in data interpretation (Sec. VI), after following the prescription in Sec. V for picking a value for  $s$ , given the adsorbate and substrate.

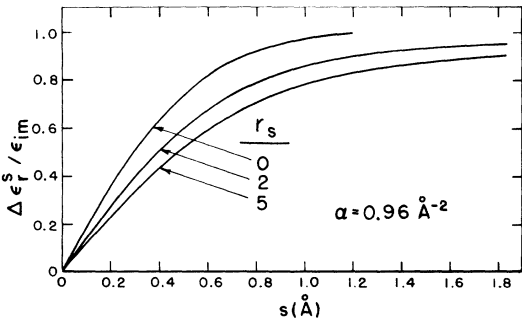


FIG. 7. Ratio of 1s hole screening energy over the point-charge image potential versus distance from surface, treating the electron-gas density parametrically. The Gaussian constant  $\alpha = 0.96 \text{ \AA}^{-2}$  is the optimal choice for a single Gaussian approximation to a hydrogen 1s orbital.

## B. Molecular-orbital states

In data analysis of photoemission spectra from adsorbed or condensed molecules, as discussed in Sec. VI, knowledge of the screening energy of a nonbonding MO hole state in the adsorbate is often required.<sup>15</sup> It is thus of considerable importance, in analogy with Sec. III B, to study the theoretical screening energy for MO holes outside the surface. Again we will consider the prototype  $H_2$  molecule. As shown in Fig. 8, there are two different natural orientations of the molecule with respect to the surface, each of which may have different screening energies. This fact may be useful in determining molecular orientations.

In the coordinate system labeled in Fig. 8, the MO for the parallel orientation is formed from the 1s Gaussian atomic orbitals

$$\phi_{\parallel}(\vec{r} - \vec{R}_1) = (2\alpha/\pi)^{3/4} e^{-\alpha(x+a/2)^2} e^{-\alpha y^2} e^{-\alpha(z-s)^2}, \quad (31)$$

$$\phi_{\parallel}(\vec{r} - \vec{R}_2) = (2\alpha/\pi)^{3/4} e^{-\alpha(x-a/2)^2} e^{-\alpha y^2} e^{-\alpha(z-s)^2};$$

and for the perpendicular orientation from

$$\phi_{\perp}(\vec{r} - \vec{R}_1) = (2\alpha/\pi)^{3/4} e^{-\alpha(x^2+y^2)} e^{-\alpha(z-s)^2}, \quad (32)$$

$$\phi_{\perp}(\vec{r} - \vec{R}_2) = (2\alpha/\pi)^{3/4} e^{-\alpha(x^2+y^2)} e^{-\alpha(z-s-a)^2}.$$

After a bit of rearrangement the MO hole charge densities, from Eqs. (17), (31), and (32) are

$$\rho_{\parallel}(\vec{r}) = (2\alpha/\pi)^{3/2} e^{-2\alpha y^2} e^{-2\alpha(z-s)^2} \times e^{-2\alpha(x^2+a^2/4)} (1 + \cosh 2\alpha x a) \quad (33)$$

and

$$\rho_{\perp}(\vec{r}) = \frac{1}{2} (2\alpha/\pi)^{3/2} e^{-2\alpha(x^2+y^2)} e^{-2\alpha(z-s)^2} \times (1 + e^{-4\alpha a(a/2-z+s)} + 2e^{-2\alpha a(a/2-z+s)}). \quad (34)$$

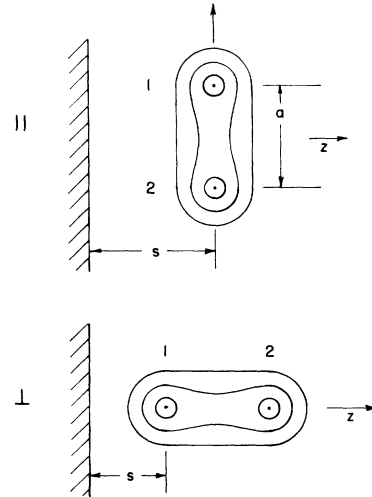


FIG. 8. Illustration of the geometrical alternatives for an adsorbed  $H_2$  molecule.

The two-dimensional Fourier transforms of the charge densities are defined by Eq. (11). From Eqs. (33) and (11), it can be shown that

$$\rho_{\parallel}(\vec{q}, z) = f_{\parallel}(z) e^{-\alpha a^2/2} e^{-q^2/8\alpha} \times [1 + e^{\alpha a^2/2} \cos(\frac{1}{2} qa \cos\phi)],$$

with

$$f_{\parallel}(z) \equiv (2\alpha/\pi)^{1/2} e^{-2\alpha(z-s)^2}. \quad (35)$$

Similarly from Eqs. (11) and (34)

$$\rho_{\perp}(\vec{q}, z) = f_{\perp}(z) e^{-q^2/8\alpha},$$

with

$$f_{\perp}(z) = \frac{1}{2}(2\alpha/\pi)^{1/2} e^{-2\alpha(z-s)^2} \times (1 + e^{-4\alpha a(a/2+s-z)} + 2e^{-2\alpha a(a/2+s-z)}). \quad (36)$$

For simplicity consider the perfect-conductor surface screening energy given by Eq. (24). With either  $\rho_{\parallel}$  or  $\rho_{\perp}$  [Eqs. (35) or (36)], Eq. (24) can be reduced to a single quadrature, using the integral representation for  $J_0$ , i.e.,  $\int_0^{2\pi} d\phi \cos(b \cos\phi) = 2\pi J_0(b)$ . After some tedious but straightforward algebra, the final results are

$$\Delta\epsilon_{r,\parallel}^s = \frac{e^2 e^{-\alpha a^2}}{8(1+S)^2} \int_0^{\infty} dq \left[ \left( \frac{2+e^{\alpha a^2}}{2} \right) + 2e^{\alpha a^2/2} J_0(qa/2) + \frac{e^{\alpha a^2}}{2} J_0(qa) \right] \times \left| e^{-qs} \left[ 1 - \Phi \left( \frac{q-4\alpha s}{(8\alpha)^{1/2}} \right) \right] + e^{+qs} \left[ 1 - \Phi \left( \frac{q+4\alpha s}{(8\alpha)^{1/2}} \right) \right] \right|^2 \quad (37)$$

and

$$\Delta\epsilon_{r,\perp}^s = \frac{e^2}{32(1+S)^2} \int_0^{\infty} dq \left\{ e^{-qs} \left[ 1 - \Phi \left( \frac{q-4\alpha s}{(8\alpha)^{1/2}} \right) \right] + e^{+qs} \left[ 1 - \Phi \left( \frac{q+4\alpha s}{(8\alpha)^{1/2}} \right) \right] + e^{-\alpha(s+a)} \left[ 1 - \Phi \left( \frac{q-4\alpha(s+a)}{(8\alpha)^{1/2}} \right) \right] + e^{\alpha(s+a)} \left[ 1 - \Phi \left( \frac{q+4\alpha(s+a)}{(8\alpha)^{1/2}} \right) \right] + 2e^{-\alpha a^2/2} \left\{ e^{-\alpha(s+a/2)} \left[ 1 - \Phi \left( \frac{q-4\alpha(s+a/2)}{(8\alpha)^{1/2}} \right) \right] + e^{\alpha(s+a/2)} \left[ 1 - \Phi \left( \frac{q+4\alpha(s+a/2)}{(8\alpha)^{1/2}} \right) \right] \right\} \right\}^2. \quad (38)$$

Equations (37) and (38) have been evaluated for a number of different choices of parameters. The ratio  $\Delta\epsilon_r^s/\epsilon_{\text{im}}$  versus  $s$  is shown in Fig. 9 for the not unreasonable choice of parameters  $\alpha = 0.96 \text{ \AA}^{-2}$  and  $a = 0.8 \text{ \AA}$ . Also included are the imperfect-screening results in which the factor  $(1+2q^2/\kappa^2)^{-1}$ , evaluated at  $r_s = 4$  is inserted into the integrands of Eqs. (37) and (38). As is apparent, significantly different ( $\sim 40\%$  variation) screening energies are obtained for the MO state, depending on orientation, when  $s \lesssim 1 \text{ \AA}$ , as expected for adsorbed species. The fact that  $\Delta\epsilon_{r,\perp}$  is smaller than  $\Delta\epsilon_{r,\parallel}$ , for the same value of  $s$ , is quite reasonable since the center of gravity of the perpendicularly oriented molecule charge is farther from the surface. Thus it seems likely that assigning identical relaxation energies to different nonbonding MOs of an adsorbed molecule could be misleading if any subsequent conclusions are sensitive to discrepancies in screening energies which are of order 50%.

## V. LOOSE ENDS

Throughout this paper, various questions deserving of answers have arisen. Many of these have been relegated to this section since their inclusion

in the main text was not essential for the principal message. The deferred questions are as follows.

### A. Self-consistency

It was mentioned after Eq. (2) that the self-energy would be approximated as  $\Sigma(\vec{r}, \vec{r}'; \epsilon; \epsilon_a + \Delta\epsilon_r) \approx \Sigma(\vec{r}, \vec{r}'; \epsilon_a)$ , thus neglecting self-consistency to this order. This is in contrast with recent work by Hodges<sup>35</sup> in which the importance of self-con-

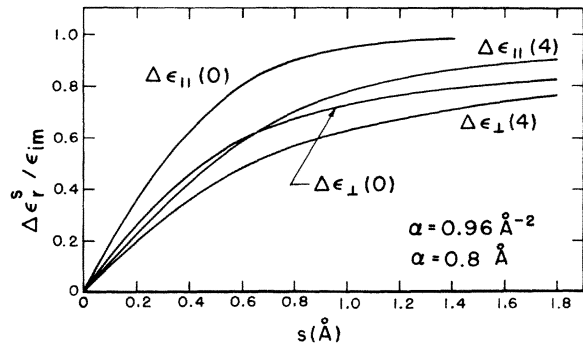


FIG. 9. Ratio of molecular screening energy over image potential versus distance from surface for the parallel and perpendicular orientations shown in Fig. 8. The numbers in parenthesis are the  $r_s$  values.

sistent calculations of  $\Sigma$  was stressed. However, Hodges was concerned with the problem of positron surface states which extend into the vacuum. These states are bound to the surface solely by the imagelike potential obtained from  $\Sigma(\vec{r}, \vec{r}'; \epsilon)$  and thus a self-consistent solution for  $\Sigma(\vec{r}, \vec{r}'; \epsilon)$  is necessary if the resulting eigenvalues are to be treated with confidence. On the other hand, for the hole screening problem, a strong ion core potential is already included in the definition of  $\phi_a(\vec{r})$  and the relatively weak image potential is just a small ( $\approx 10\%$ ) correction to the hole potential and thus eigenvalue. Consequently, a non-self-consistent perturbation calculation should be adequate.

#### B. Itinerant holes

Already in the discussion of the  $s \rightarrow \infty$  limit of the  $H_2$  bulk screening energy, several points have been made concerning the relative hole hopping versus hole screening time scales and their importance in the apparent screening-energy shifts. (I am grateful for some informative discussions with J. R. Schrieffer). A nontrivial point arises in the case of chemisorbed entities where the system wave functions are of the form<sup>60</sup>

$$\psi_{\text{system}}(\vec{r}) = \psi_{\vec{k}}(\vec{r}) + \sum_{\vec{k}'} \frac{\phi_a(\vec{r}) V_{a\vec{k}'}}{\epsilon - \epsilon(\vec{k}')}.$$

Here  $\psi_{\vec{k}}$  is a substrate wave function with energy  $\epsilon(\vec{k})$ , normalized over a large volume,  $\phi_a$  is an adsorbate wave function introduced in Eq. (3), and  $V_{a\vec{k}'}$  is the adsorbate-substrate hopping integral. The question raised here is what is the justification for treating adsorbate relaxation with  $V_{a\vec{k}'} = 0$ , resulting in a state  $\phi_a(\vec{r})$  which relaxes as if the hole is for all times localized at the adsorbate center, when in fact the system eigenfunctions are delocalized over the whole substrate and adlayer? Then almost as an afterthought, the relaxation shifted energy level is broadened by  $V_{a\vec{k}'}$ , which in the simplest virtual-level model yields local density of states on the adatom

$$\rho_{aa}(\epsilon) = \frac{1}{\pi} \frac{\Delta_a}{(\epsilon - \epsilon_a - \Delta\epsilon_r)^2 + \Delta_a^2},$$

with  $\Delta_a \approx \pi N(\epsilon_F) \langle |V_{a\vec{k}'}|^2 \rangle$  and  $N(\epsilon_F)$  the substrate density of states at the Fermi level. The physics behind this procedure can be seen from a wave-packet point of view. Suppose a hole, which is a nonstationary system state, is created on the adatom. The substrate electron gas will respond to this hole in a time of order  $\omega_p^{-1}$ . Although the hole is itinerant, as it is a wave packet, it will remain on the adsorbate for a time  $\sim \hbar/\Delta_a$ . Since  $\Delta_a \ll \hbar\omega_p$  (typically  $\Delta_a/\hbar\omega_p \approx 0.1$ ), the electron gas will have had sufficient time to completely relax before the hole or wave packet starts meandering

through the substrate. Thus the relaxation first, broadening second procedure can be seen to make physical sense in the case in which the level width of the virtual state (or narrow band) is small relative to the bandwidth and thus the plasmon energy of the relaxing electrons.

#### C. Nonpolarizable holes

By considering only the  $x=a$  term in the sum in Eq. (3), we have omitted any effects due to the polarization of the hole. Pictorially, from Fig. 1, this implies that the intermediate-state hole propagator is determined in a way which is independent of the particular induced density fluctuation within the solid. In other words, there is no feedback, in which the induced density fluctuation alters the propagation of the hole which induced the density fluctuation in the first place.

To get a feel for the significance of this approximation, consider Eq. (6) rearranged as

$$\Delta\epsilon_r^b = \int \frac{d^3q}{(2\pi)^3} \left( \frac{4\pi e^2}{q^2} \right) \frac{i}{2\pi} \int d\omega \left( \frac{1 - \epsilon(q, \omega)}{\epsilon(q, \omega)} \right) \times \sum_x \frac{|\langle a | e^{i\vec{q}\cdot\vec{r}} | x \rangle|^2}{\epsilon_a - \omega - \epsilon_x}. \quad (39)$$

Expanding the exponential in the matrix element and keeping only the first two terms, the summation in Eq. (39) is

$$\begin{aligned} \sum_x &\approx \sum_x \frac{|\langle a | x \rangle|^2}{\epsilon_a - \omega - \epsilon_x} + q_x \sum_x \frac{|\langle a | z | x \rangle|^2}{\epsilon_a - \omega - \epsilon_x} \\ &= -\frac{1}{\omega} + \frac{q}{e^2} \alpha(\epsilon_a - \omega), \end{aligned} \quad (40)$$

where  $\alpha(\epsilon_a - \omega)$  is the dynamic polarizability of the impurity ion. The first term in Eq. (40) has been treated in the text. The polarization term couples the dynamics and spatial extent of the hole with the dynamics of the responding electron gas through the  $\omega$  integral

$$\sim \int d\omega \left( \frac{1 - \epsilon(q, \omega)}{\epsilon(q, \omega)} \right) \alpha(\epsilon_a - \omega).$$

A similar exercise can be carried out for the adsorbed species, in which case a formula would be obtained which is an ion-surface analog of a parallel-plate Lifshitz formula. As a trivial example, consider hydrogen. If  $V_{a\vec{k}'} = 0$ , then  $\alpha = 0$  necessarily, and this correction is irrelevant.

#### D. Hole-image plane separation

In order that the screening-energy theory presented here can be used for real data interpret-

tation, a prescription which relates  $s$ , the distance between the adsorbate center and the effective image plane, to an experimentally accessible separation must be given. Low-energy electron-diffraction (LEED) studies provide numbers which may be the distance between the adsorbate ion core and the first plane of substrate ion cores,<sup>61</sup> which we call  $z_{\text{LEED}}$ . Appelbaum<sup>62</sup> has noted that self-consistent calculations on both jellium<sup>63</sup> and pseudopotentialized Na indicate that the effective image plane should be located at a position where the substrate electron charge density tailing into the vacuum has fallen to about  $\frac{1}{3}$  its average bulk value. Theoretically this value, call it  $z_{1/3}$ , can be given with respect to a convenient origin, say at the last substrate ion core layer. Consequently the value of  $s$ , for a given adsorbate-substrate combination, to use in the present theory is

$$s = z_{\text{LEED}} - z_{1/3}, \quad (41)$$

which will tend to be a small number. If electron-density profiles from jellium calculations are used, then  $z_{1/3}$  is usually given with respect to the jellium step edge, in which case  $d/2$  must be added to  $z_{1/3}$ , with  $d$  the substrate interplanar spacing.

## VI. DATA INTERPRETATION

One of the aims of photoelectron spectroscopy of adsorbates (and implanted impurities<sup>9</sup>) is to be able to determine chemical and bonding shifts in electron energy levels by comparing gas-phase and solid-state spectra. A meaningful comparison is not straightforward since the gas-phase result is displaced, upon adsorption or implantation, by chemical, bonding, surface-dipole, and relaxation shifts. In spite of the fact that this has been discussed at some length in the literature,<sup>9,10,15,64</sup> considerable misunderstanding still abounds and one frequently hears the total shift between gas and solid phase being identified as a relaxation shift. Another "problem" relates to referencing binding energies with respect to vacuum or Fermi levels. In fact neither procedure allows one to make direct comparisons with gas-phase results in a way in which chemical shifts can be extracted, without knowing more about the surface barrier than the work function.

To visualize the situation, consider a core-state electron with a binding energy  $\epsilon_b$  in the gas-phase atom outside a semi-infinite solid, shown in Fig. 10. (We require a semi-infinite solid in order to avoid the problems discussed by Estrup and Quinn<sup>65</sup> regarding the difference between the electrostatic potential just outside the solid and the "vacuum potential.") Upon ionization with photons of energy  $h\nu$ , the ejected electron possesses kinetic energy

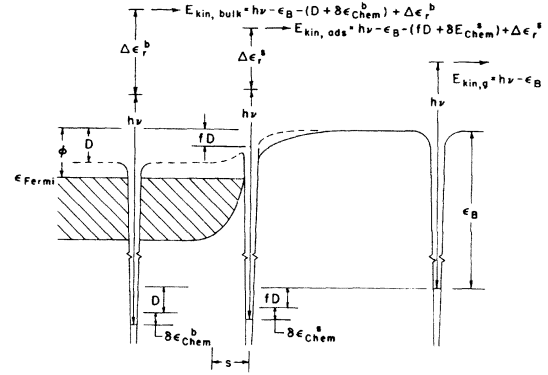


FIG. 10. Electrostatic-potential diagram relevant to photoejection of a core electron in a gaseous, adsorbed, and implanted atom, with respect to a surface of a metal with dipole potential  $D$  and work function  $\phi$ . The relation between ejected electron kinetic energy and system properties for the three cases is shown in the figure and discussed in the text.

$$E_{\text{kin, g}} = h\nu - \epsilon_b. \quad (42)$$

As the atom approaches the surface it enters the electrostatic field of the dipole barrier which raises the binding energy of the atomic electrons, with respect to the vacuum zero. As depicted in Fig. 10, the lowering of the level (increase in  $\epsilon_b$ ) for an atom a distance  $s$  from the surface is  $f(s)D$ , where  $D$  is the total dipole barrier at the surface,<sup>63</sup> the difference between the average electrostatic potential deep within the solid and far out into the vacuum for jellium, and  $f(s)$  is the fraction of the dipole potential which has been penetrated by the atom.<sup>66</sup> This dipole may be just the intrinsic dipole of the pure substrate or it may include contributions due to the adlayer. An additional chemical shift  $\delta\epsilon_{\text{chem}}$  of the type discussed by Siegbahn<sup>1</sup> may also raise or lower the binding energy. When an electron is photoejected from such an adsorbed atom, the screening energy gained by the substrate electrons is balanced by  $\Delta\epsilon_r^a$ , the extra-atomic relaxation energy which requires an upward shift of the ejected-electron kinetic energy, now given by

$$E_{\text{kin, ads}} = h\nu - \epsilon_b - [f(s)D + \delta\epsilon_{\text{chem}}(s)] + \Delta\epsilon_r^a. \quad (43)$$

Lastly, if the adsorbate completely penetrates the dipole layer and sees the bulk screening energy, then the atom is implanted and after photoejection will have kinetic energy

$$E_{\text{kin, bulk}} = h\nu - \epsilon_b - [D + \delta\epsilon_{\text{chem}}(\text{bulk})] + \Delta\epsilon_r^b. \quad (44)$$

By comparing Eqs. (42)–(44), it is apparent that nothing can be learned about  $\delta\epsilon_{\text{chem}}$  from a comparison of experimentally measured values of  $E_{\text{kin, g}}$  and  $E_{\text{kin, ads}}$  without independent knowledge of both the dipole part of the surface barrier and

also  $\Delta\epsilon_r$ . Attempts are often made to deal with this problem by subtracting a work function, in which case the terminology "referencing with respect to the Fermi level" rather than with respect to the vacuum level is introduced. This is a harmless exercise but does not help at all in obtaining any meaningful number from a gas-surface comparison. Knowing  $\Delta\epsilon_r^s$ , which is the aim of this paper, it is then possible to infer the total chemical shift,  $f(s)D + \delta\epsilon_{\text{chem}}$ , from comparisons of gas and solid spectra.

## VII. SUMMARY

A linear-response theory for calculating screening or extra-atomic relaxation energies of localized holes on atoms or molecules implanted in or adsorbed on free-electron gas solids has been presented. It was found that as the spatial extent of the hole became comparable with the screening length of the electron gas, the screening energy was considerably reduced from the point-hole value. Bonding effects which lead to more delocalized wave functions did not greatly alter the screening energy, at least for  $\text{H}_2$ , the simplest prototype molecule. The influence of chemical

bonding between the impurity and the host on the screening energy of the bonding orbital was not investigated. The relation between the classical image potential and the extra-atomic screening energy for a hole on an adsorbed atom or molecule was established. In conductors with nonzero screening lengths, the surface screening energy is always smaller than for a perfect conductor. Possible differences in  $\Delta\epsilon_r$ , depending on adsorbed molecule orientation were illustrated, again for  $\text{H}_2$ . The connection between gas-phase and adsorbed or absorbed atom photoelectron spectra was illustrated and the fact that experimental shifts are combinations of chemical and relaxation shifts was emphasized. Little direct comparison with experimental data has been given here as that will be the subject of a forthcoming paper.<sup>64</sup>

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$$V_{\text{in}}(\vec{r}', \omega) = e^2 \int \rho_{\text{in}}(\vec{r}, \omega) / |\vec{r} - \vec{r}'| d^3r,$$

$$\rho_{\text{in}}(\vec{q}, \omega) = \{[1 - \epsilon(q, \omega)] / \epsilon(q, \omega)\} \rho_0(\vec{q}, \omega),$$

and

$$e^2 / r_{12} = \int \frac{d^3q}{(2\pi)^3} (4\pi e^2 / q^2) e^{i\vec{q} \cdot \vec{r}_{12}},$$

combining these relations and performing the functional derivative yields Eq. (4).

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<sup>49</sup>Or if off-diagonal elements were included, by

$$\rho_{\text{ax}}(\vec{q}) = \int d^3r \phi_{\vec{a}}^*(\vec{r}) \phi_x(\vec{r}) e^{i\vec{q} \cdot \vec{r}}.$$

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