

Core holes in chemisorbed atoms

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The self-consistent atom-jellium model developed previously for the study of atomic chemisorption on simple metals is used here to study extra-atomic shifts in core-electron binding energies. Within a single internally consistent model, we calculate both the relaxation shift and chemical shifts due to charge transfer, atomic compression, the surface dipole layer, and metal-adatom bonding. We also study in detail the accuracy of purely atomic and purely metallic approximations to relaxation in the combined metal-adatom system.

I. INTRODUCTION

We discuss in this paper the change in the binding energy of an atomic core electron which occurs when the atom is allowed to chemisorb on the surface of a simple metal. This energy change can be determined via x-ray photoemission of the core electron.¹ We consider changes which take place prior to the removal of the electron (chemical or initial-state effects) as well as those associated with the screening of the core hole (relaxation or final-state effects). In addition to the energy shifts associated with these effects, our calculations provide a detailed description of the microscopic electron density changes which cause them. We shall refer to all effects caused by the interaction with the metal as extra-atomic, even if the spatial interior of the atom is involved.²

The primary motivation for this study is the fact that extra-atomic binding energy changes are large and must be understood in order to profit fully from x-ray photoemission measurements. The atom-jellium model³⁻⁶ we have developed for the study of atomic chemisorption on simple-metal surfaces provides us with a powerful analytical tool which was not available in earlier studies of this problem. The analysis of extra-atomic effects on core levels within this model of chemisorption is particularly interesting because the model, while both conceptually transparent and solvable, possesses the essential physical and chemical content of the problem. The lower symmetry of the chemisorption geometry, as compared with that of impurity sites inside a metal, allows us to study a wider variation in the chemical environment of the excited atom than in the impurity case. Thus, for example, we can follow the behavior of a core level, both before and after the removal of an electron, as the atom is moved through the surface dipole layer of the metal. The fact that our analysis of the atom-jellium model involves no assumptions of spherical symmetry etc. permits us to extract the full physical and chemical content of the model.^{3,4}

To make the general distinction between chemical and relaxation effects more concrete, consider a specific example. In Fig. 1 we show the valence state density of sodium chemisorbed on a high-density simple metal. The fundamental peak in each of the two spectra in this figure is derived from the sodium 3s level. It is broadened by the formation of the chemisorption bond and its initial energy position above the Fermi level of the metal indicates that the atomic level has emptied; these changes result in chemical shifts of the core levels. When an electron is removed from the sodium core, the attractive electrostatic potential created by the hole (equivalently, the reduced screening of the nucleus) lowers the valence resonance through the Fermi level, as shown in the figure, so that in this case the principal final-state effect is the reoccupation of the atomic level which was emptied in the formation of the ionic chemisorption bond; it is the charge which reoccupies this level that screens the core hole. The chemical

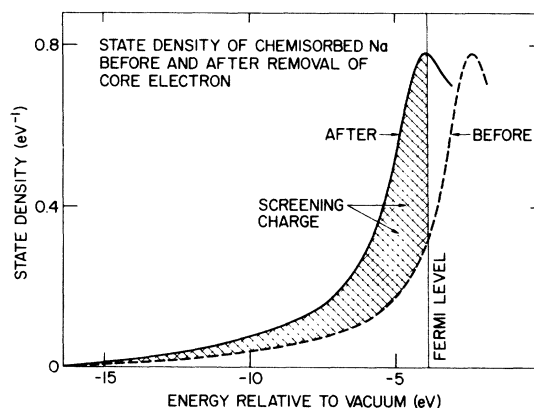


FIG. 1. State density of chemisorbed Na before and after removal of 2s core electron. (Curves shown represent the differences between the total state density of the metal-adatom system and that of the bare metal.) High-density ($r_s = 2$) substrate. Metal-adatom separation minimizes total energy of ground state (see Ref. 29). Discrete portion of spectrum not shown.

shift of the 2s core level in this example is -1.0 eV (a binding energy increase); the relaxation shift is 4.5 eV (a binding energy decrease). As this example suggests, the energy position of the resonance energy and its sensitive dependence on the occupation of the resonance make the self-consistent-field aspect of our atom-jellium model particularly important for the study of this problem.

There has been a variety of work done previously on different aspects of the core-level binding problem. Most of this work was concerned with bulk solids, and dealt with either impurity atoms in metals or the metal atoms themselves.⁷ This work is discussed in another paper⁸ by us which focuses on solids. Previous treatments⁹⁻¹¹ in the literature for extended metal surfaces are basically perturbative and essentially independent of the factor which we find to be most important, the atomic number of the excited atom.¹² In addition to dealing with surfaces, the focus of our work is the nature of the fully developed (in time) screening charge, the conceptual picture most useful for describing it and, in particular, its variation with the atomic number of the atom being excited.

The balance of the paper is organized as follows. In Sec. II we describe our calculations, the model on which they are based and the numerical results we obtain. In Sec. III we interpret these results in terms of two limiting conceptual models, purely metallic screening and purely atomic screening. After discussing the extent to which our results provide a picture that extends beyond the particular systems we have studied in detail, we present, in Sec. IV, our conclusions.

II. CALCULATIONS

A. Introduction

Since the focus of our study is the difference between core-level binding in the free and chemisorbed atom, we use the identical analytical approach for both cases. In each case we perform two self-consistent calculations of the electron density and the total energy, one for the system in its normal ground-state configuration and a second for the same system with one of the core electrons removed.¹³ In the case of the chemisorbed system, the metal-adatom distance is held constant (Franck-Condon principle). The energy required to remove a core electron to infinity (i.e., to the vacuum level) is the difference in the total energy of the excited system and the unexcited system, and the screening charge is the difference in the electron densities (excluding the charge distribution of the hole itself). The calculated extra-atomic reduction of binding energy and the extra-atomic screening charge distribution are the differences

in these differences between the free and chemisorbed atoms. Thus each extra-atomic difference involves four independent self-consistent-field calculations. While this “ Δ SCF” approach¹⁴ allows us to treat the fully developed screening of the core hole in great detail, it does not permit us to follow the time evolution of the system from the unrelaxed to the relaxed state. Our calculations, therefore, lead to predictions of the energy position of the leading edge of the kinetic-energy distribution of photoemitted electrons¹⁵; they do not provide a description of the core-level line shape.

Both the initial and final states of these systems are many-electron states and as such require a theory of exchange and correlation. In all cases we use the local-density approximation to exchange-correlation effects.¹⁶ Density-functional theory¹⁶⁻¹⁹ in general and local-density theory in particular possess formal justification only for the description of the ground (initial) state. The justification we have for using the theory for systems constrained to have a core hole is the empirical evidence provided by the many successful calculations of molecular ionization potentials,²⁰ and of core excitations by Almladh and von Barth,⁷ both of which have used this approach.²¹

The metal substrate is simulated in our calculations by semi-infinite jellium; that is, the positive ion cores of the metal are smeared into a uniform semi-infinite distribution of positive charge.^{19,22} This atom-jellium model provides a detailed, realistic picture of the chemisorption bond for adatoms on simple metals. The model and the techniques we use to solve the equations it implies are described in our earlier publications^{3,4}; we review their important features here.

The equations for the electron density, $n(\vec{r})$, are¹⁶

$$\left\{-\frac{1}{2}\nabla^2 + v_{\text{eff}}[n; \vec{r}]\right\}\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (2.1a)$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 n_i, \quad (2.1b)$$

where n_i indicates the occupation of the i th (orthonormal) orbital. (We use atomic units, with $|e| = m = \hbar = 1$.) For the ground state of the metal-adatom system, $n_i = 1$ if ϵ_i is less than the Fermi energy and $n_i = 0$ otherwise; for the case of a core hole in state i , these equations are solved self-consistently with n_i set to zero. The effective potential $v_{\text{eff}}[n; \vec{r}]$ is the sum of the electrostatic potential due to all of the charges in the system and the local-density approximation²³ to the contribution of exchange and correlation. The eigenvalue spectrum $\{\epsilon_i\}$ is entirely discrete for the atomic calculations and is a mixture of discrete and continuous portions in the case of chemisorption. In solving these equations we make essentially no

approximations other than the local-density description of exchange-correlation and the jellium simulation of the metal. The electronic charge constituting both the chemisorption bond and the core-hole screening cloud is completely free to take the configuration of lowest energy; it is not restricted by assumed basis sets, the requirement of spherical symmetry in the core region, etc. In particular, the core states are free to contract around the core hole and to polarize in response to the asymmetric potential field in the metal surface region.

The local-density formalism we use to approximate exchange and correlation, due to its electron-gas origin,²³ makes its greatest errors for tightly bound core electrons. It might appear, therefore, to be a poor basis for a theory of core excitations. We avoid this difficulty by restricting ourselves to the calculation of extra-atomic differences, which are well described by the theory, because they are valence-electron effects.^{24,25} (Core-electron effects, since they are approximately the same in the free and chemisorbed atom, largely subtract out of extra-atomic differences.)

B. Numerical results

The numerical quantity of interest is the difference Δ between the core binding energy of the free atom and that of the chemisorbed atom. This extra-atomic reduction Δ in the binding energy (i.e., the reduction in going from the free to the chemisorbed atom) is, as mentioned above, the difference of two total energy differences:

$$\begin{aligned} -\Delta = & [E(\text{chemisorbed atom with core hole}) \\ & + \Phi - E(\text{chemisorbed atom})] \\ & - [E(\text{free atom with core hole}) \\ & - E(\text{free atom})]. \end{aligned} \quad (2.2)$$

We write $-\Delta$ so as to organize the terms on the right-hand side in a manner convenient for later discussion. $E(\text{chemisorbed atom})$ means in fact the total energy of the metal-adatom system, and the sum $E(\text{chemisorbed atom with core hole}) + \Phi$ is the total energy of the metal-adatom system with an adatom core electron removed to the vacuum level. The quantity Φ is the metal work function, so that $E(\text{chemisorbed atom with core hole})$ is the energy of the metal-adatom system with a core electron removed and an additional electron at the Fermi level. We define such an energy because both in an experiment with a grounded sample and in our calculations for the atom-jellium model, the creation of a core hole automatically brings another electron into the system at the Fermi level in order to preserve charge neutrality.

Since the principal motivation for the x-ray photoemission analysis of deep core levels is to probe the charge state and chemical environment of an atom through variation in core-level binding energies, we decompose the extra-atomic reduction in binding energy into two parts, the chemical shift Δ_c which reflects these properties, and the relaxation shift Δ_r :

$$\Delta = \Delta_c + \Delta_r. \quad (2.3)$$

Δ_c is usually the quantity of interest, because it contains information concerning the charge state of the atom and the way in which the atom is bonded to nearby atoms. Δ_c has nothing to do with the core excitation process *per se*; it is a property of the ground state. Δ_r , on the other hand, is the amount by which the core level is raised by the relaxation of other electrons in response to the presence of the core hole. To the extent to which the objective of core-level spectroscopy is the charge state and chemical environment of the excited atom, as opposed to the excitation process itself, its utility depends on Δ_r not being a strong function of these chemical factors.

The physical phenomena involved in the chemical and relaxation shifts are quite different. The principal contributors to the chemical shift in the context of chemisorption are charge transfer, the equilibrium position of the adatom with respect to the dipole-layer potential of the metal substrate and the compression of the extended atomic electron density into the smaller volume it occupies when the atom is bonded to the metal surface.²⁶ The principal contributors to the relaxation shift are the contraction of both core and valence orbitals in response to the reduced screening of the nuclear charge and the transfer of additional screening charge to the excited atom or its immediate vicinity. (The spatial distribution of this screening charge, due to its relative experimental inaccessibility, is a particularly interesting output of our calculations.)

The chemical and relaxation contributions to the extra-atomic reduction of core-level binding energies cannot be measured individually. The theoretical decomposition is, therefore, somewhat arbitrary. Fortunately, there appears to be a single reasonable decomposition within the theoretical framework we are using. The energy eigenvalues associated with discrete core levels in the density-functional formalism are not directly measurable.²⁷ The change in these eigenvalues with the chemical state and environment of the atom, however, appears to be exactly what the chemical shift notion is intended to identify:

$$\Delta_c = \epsilon_i(\text{chemisorbed atom}) - \epsilon_i(\text{free atom}), \quad (2.4)$$

where the state index i refers to a deep core level. In particular, we find it to be accurately approximated by the change in the electrostatic potential at the nucleus, which is frequently used as a definition of the chemical shift. This definition of the chemical shift [Eq. (2.4)] together with the unambiguous definition of the total binding energy reduction defines, by subtraction, the relaxation shift. An approximate, but independent, definition of the relaxation shift discussed in Sec. III confirms the reasonableness of our definition of the chemical shift.

The bar graph in Fig. 2 shows the chemical and relaxation shifts we have calculated for a representative set of adatoms chemisorbed on a high-density simple metal.^{28,29} The chemical shift is seen to follow the sign of the charge transfer associated with the chemisorption bond (and, therefore, the electronegativity of the adatom with respect to that of the metal surface). The relaxation shift is seen here to be positive in all cases; its magnitude follows closely the spatial extent of the screening charge distribution. (This dependence is discussed in Sec. III.)

To establish the plausibility of our results and of our interpretation, we compare our calculated extra-atomic reduction of the $1s$ binding energy in chemisorbed oxygen with a value extracted from experiment. Our reason for focusing on oxygen is the widespread experimental interest in the oxidation process and the availability of an accurate calculation of the core binding energy for the atom³⁰⁻³³ [$I_A(\text{calc})$]. We use a value for the $1s$ binding energy referred to the Fermi level [$I_F(\text{meas})$] measured by Brundle³⁴ for oxygen on aluminum, which we refer to the vacuum level by adding the measured value of the aluminum work

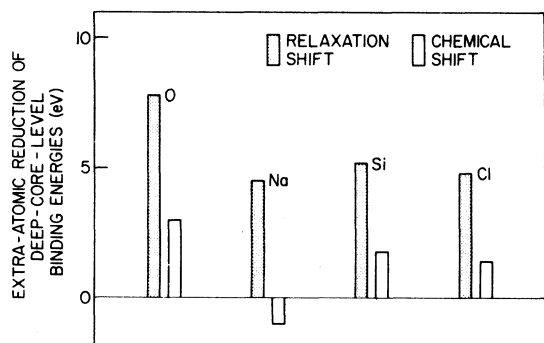


FIG. 2. Decomposition of extra-atomic reduction of deep-core-level binding energy into its two components. Single atoms of O, Na, Si, and Cl chemisorbed on high-density ($r_s = 2$) simple-metal surface. Metal-adatom separations for Na, Si, and Cl are given in Ref. 29; oxygen was placed inside the metal (see text). Hole state is $1s$ for O, $2s$ for Na, Si, and Cl.

function³⁵ [$\Phi(\text{meas})$]. Since experimental evidence suggests that oxygen penetrates the surface of simple metals,³⁶⁻³⁸ we use the atom-jellium model to calculate Δ for a dissolved atom (rather than one which remains on the surface). Because the effects of replacing the positive ions of the substrate by a uniform distribution of positive charge are not negligible for atom positions inside the metal, we add to our value of $\Delta(\text{atom-jellium})$ an estimate of the change in Δ due to our jellium simulation of the metal. We obtain this estimate [$\delta\Delta(\text{pseudopotential})$] using the first-order perturbation-theory formula given in the Appendix in conjunction with an ion-core pseudopotential appropriate to aluminum³⁹; the oxygen is taken to reside in an interstitial (tetrahedral or octahedral) position. Our comparison between measured and calculated values for Δ is therefore

$$\begin{aligned}\Delta(\text{meas}) &= I_A(\text{calc}) - [I_F(\text{meas}) + \Phi(\text{meas})] \\ &= 545.9 \pm 0.5 \text{ eV} - [(531.8 + 4.2) \text{ eV}] \\ &= 9.9 \pm 0.5 \text{ eV}, \\ \Delta(\text{calc}) &= \Delta(\text{atom-jellium}) + \delta\Delta(\text{pseudopotential}) \\ &= (10.8 - 1.3) \text{ eV} = 9.5 \text{ eV}.\end{aligned}$$

It should be observed that the contribution associated with the discreteness of the host lattice [$\delta\Delta(\text{pseudopotential})$] is comparable in magnitude to the difference between the measured and calculated values of Δ . In noting the good agreement between theory and experiment, we recall the fact that there are no adjustable quantities in our calculation.

III. INTERPRETATION

A. Atomic character of screening by the metal

In this section we examine the internal structure of the charge distribution which forms to screen the core hole and draw qualitative inferences which, we believe, are not restricted to the four specific systems we have studied. We consider the question of whether the screening charge distribution is fundamentally metallic or atomic in character. The top half of Fig. 3 gives contour plots of the extra-atomic screening charge density calculated using the atom-jellium model for Na and Cl. The extra-atomic screening charge distribution is defined by the following difference of differences [$n(\vec{r})$ is electron number density]:

$$\begin{aligned}n(\vec{r}; \text{extra-atomic}) &= [n(\vec{r}; \text{chemisorbed atom with core hole}) \\ &\quad - n(\vec{r}; \text{chemisorbed atom})] \\ &\quad - [n(\vec{r}; \text{free atom with core hole}) \\ &\quad - n(\vec{r}; \text{free atom})].\end{aligned}\quad (3.1)$$

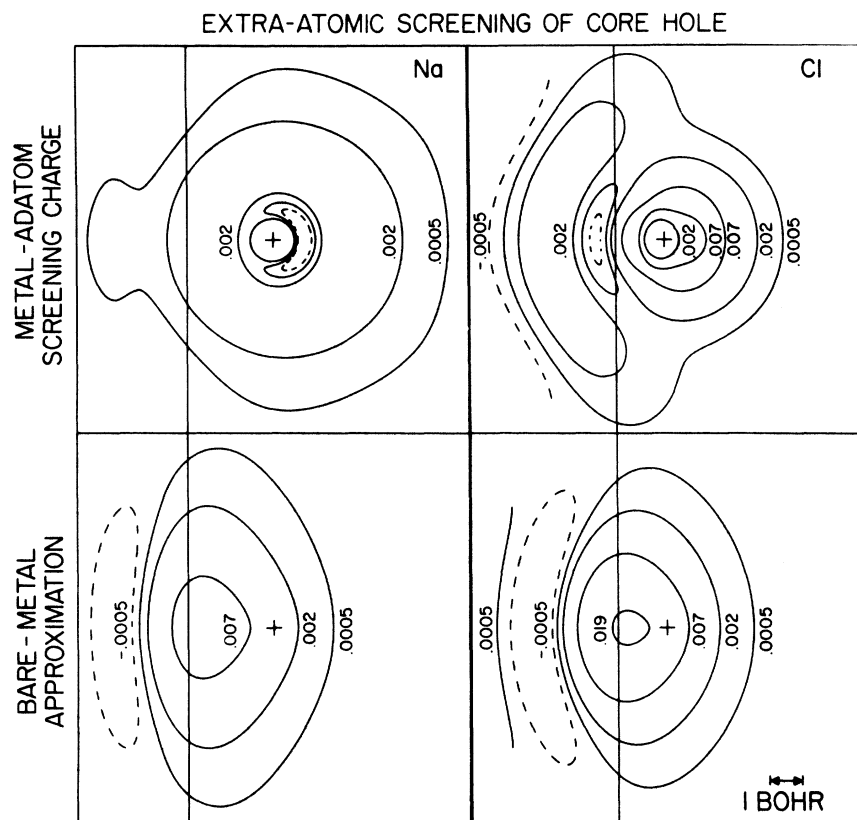


FIG. 3. Contours of constant electron density showing, in the upper plots, the spatial distribution of extra-atomic screening charge for Na and Cl chemisorbed on a high-density ($r_s = 2$) simple-metal surface, and in the lower plots, the linear dielectric response of the bare metal to point charges at the same distances. Metal to left-hand side; vacuum to right-hand side. Adatom nucleus indicated by "+". Solid vertical line indicates positive-background edge. For computational convenience, contours are not shown outside inscribed circle of each square. Contour values used were ± 0.019 , ± 0.007 , ± 0.002 , and ± 0.0005 . For reference, the bulk metal density is 0.03 electrons/bohr³. Contours in core regions have been deleted for clarity. Hole state is 2s. Metal-adatom separations obtained as described in Ref. 29.

As we would expect for a screening charge distribution, $n(\vec{r}; \text{extra-atomic})$ contains one electron (i.e., integrates to unity). This is so because the difference between the two atomic densities in Eq. (3.1) integrates to unity, while the difference between the chemisorption densities integrates to zero, since $n(\vec{r}; \text{chemisorbed atom with core hole})$ corresponds to the case in which there is an additional electron at the Fermi level to compensate the charge of the core hole [see the discussion of Eq. (2.2) above].

The screening of a core hole is sometimes visualized as the linear response of the metal to a positive point charge at the position of the atomic nucleus. This approximation to the screening is displayed in the bottom half of Fig. 3. These linear-response results were obtained using the same analytical apparatus employed to study the atom-jellium model. That is, the electron density is calculated in the presence of a small positive point charge and the bare-metal density is subtracted; this density difference (i.e., the screening charge) is then scaled up by the inverse of the magnitude of the point charge. The two linear-response plots differ only in the separation of the point charge and the jellium surface.

The spherical character of the (extra-atomic) screening charge for Na given by the atom-jellium calculations (upper left-hand portion of Fig. 3) is consistent with the idea, suggested by Fig. 1, that the screening charge resides in the lowest otherwise unoccupied atomic orbital. The case of Cl is quite different. As seen in Ref. 4, the 3p resonance in Cl lies well below the Fermi level (reflecting the initial-state charge transfer that takes place) and thus this resonance is unable to accept any final-state screening charge,⁴⁰ in contrast to the case of Na. We should note that we are not asserting that the filled resonance necessarily corresponds to what could be thought of as the full complement of six electrons in the 3p shell, because as discussed by Pendry,⁴¹ some part of the spectral weight of the 3p level has been mixed into states of energies extending far above the Fermi level. This spectral weight is however largely unavailable to accommodate screening charge, and so we can think of the 3p shell as filled for purposes of our discussion.⁴⁰ The several positive contours immediately surrounding the core do not represent additional screening charge but rather indicate a displacement toward the core of the charge transferred to the Cl atom during chemisorption. (In the initial state,

this additional charge is strongly polarized toward the metal, with the peak in density located just to the right of the small negative contour in the Cl map in Fig. 3.) The additional Cl final-state screening charge in fact lies in the metal, and is represented by the kidney-shaped contour in Fig. 3.

The Na screening charge is not well described by the linear-response picture, and even the Cl screening charge that resides in the metal is not, except insofar as it also exhibits an elongation parallel to the surface. Note that the off-centeredness of the linear-response screening charge is consistent with the fact that if the point charge is removed to large distances from the metal surface, the screening charge remains on the surface, becoming the image-charge distribution. We wish to emphasize that the linear-response picture fails, not because it is linear, but because the metallic dielectric function lacks the structure of the atom. (We have tested the linearity of the atom-jellium response by removing fractions of core electrons.) However, even though the purely metallic screening does not capture many of the important features of the screening charge, it remains possible that it provides a useful estimate of the extra-atomic relaxation energy. This possibility occurs because the extra-atomic relaxation energy is to a good approximation (see below) one-half of the electrostatic potential at the position of the nucleus due to the extra-atomic screening charge, which in turn is proportional to the average inverse distance of this screening charge from the point charge. Such an average is not sensitive to the internal structure of the screening charge.⁴²

Whereas Fig. 3 compares the response of the combined metal-adatom system to the bare-metal response, Fig. 4 compares the metal-adatom response to the other limiting qualitative notion of the screening charge, the purely atomic response. The model for the screening charge referred to in Fig. 4 as the "excited-atom approximation" is obtained by subtracting the electron density of the ion (i.e., the free atom with a core hole) from that of the excited atom, that is, an atom in which a core electron has been transferred (also self-consistently) to the lowest unoccupied valence orbital. Figure 4 shows that the atomic model⁷ is quite adequate for Na and Si; for Cl, the effective filling of the valence shell in the initial state renders the model inappropriate. The second hump in the radial distribution (the screening charge at distances between r and $r+dr$ from the adatom nucleus divided by 4π) for Cl corresponds to the kidney-shaped contour in Fig. 3. In this case the added screening charge can be viewed (as noted above) as residing in metal states, or alternatively in a directional hybrid of atomic Cl $4s$ and $4p$ states.

B. Approximate formula for relaxation energies

Here we derive a simple formula relating the relaxation energy directly to the screening-charge distribution. Only the simple derivation we give of the formula is new; the same result was previously obtained by Hedin and Lundqvist¹⁵ (cf. also Almladh and von Barth⁷). The formula represents for the density-functional formalism what the "polarization potential" formula of Hedin and Johansson⁴³ represents for the Hartree-Fock formalism. For the present work the formula performs two logical

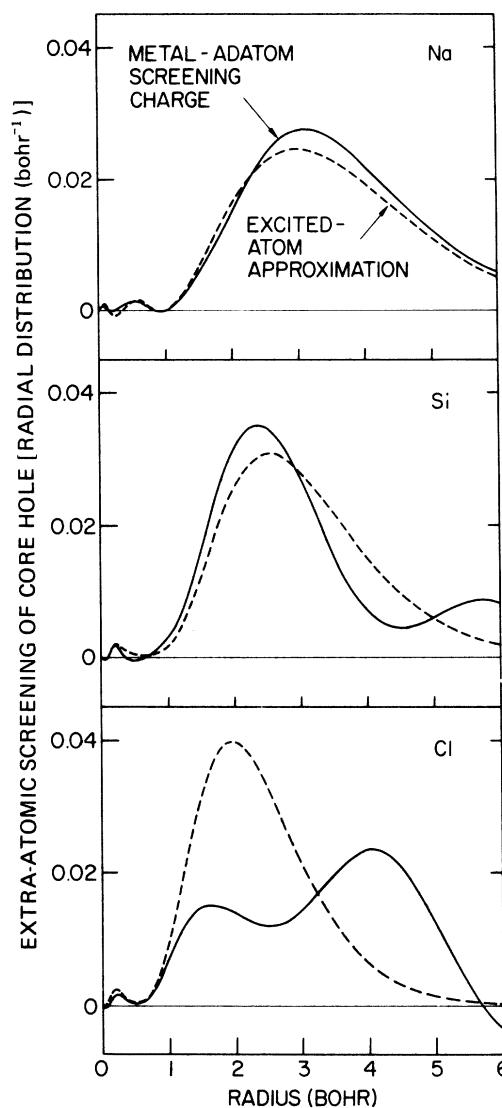


FIG. 4. Radial distribution of extra-atomic screening charge (charge between r and $r+dr$ divided by 4π) for Na, Si, and Cl chemisorbed on high-density ($r_s=2$) simple-metal surface. Hole state is $2s$. Metal-adatom separations given in Ref. 29. Distance measured from adatom nucleus.

functions: it allows us quantitatively to assess the accuracy of the excited-atom approximation and the independent definition of the extra-atomic relaxation shift it provides constitutes a check of our definition of the chemical shift (see Sec. II B).

Our derivation begins with the transition-state technique introduced by Slater.⁴⁴ The eigenvalues ϵ_i arising in density-functional theory are the derivatives of the total energy of the system with respect to the corresponding occupation number⁴⁴ n_i [cf. Eq. (2.1)]:

$$\epsilon_i = \frac{\partial E}{\partial n_i}. \quad (3.2)$$

Within the Δ SCF framework, the energy required to remove an electron from the i th orbital to infinity is $E(n_i=0) - E(n_i=1)$, which can be written, using Eq. (3.2),

$$E(n_i=0) - E(n_i=1) = \int_1^0 dn'_i \epsilon_i(n'_i). \quad (3.3)$$

Slater's transition-state technique is the approximation of such integrals by the "midpoint" numerical quadrature formula⁴⁵

$$E(n_i=0) - E(n_i=1) \approx -\epsilon_i(n_i = \frac{1}{2}). \quad (3.4)$$

(Since the midpoint formula correctly integrates only linear variations, deviations from the transition-state approximation are a measure of the nonlinearity of the system's response to hole creation or other changes of occupation number.)

Applying the transition-state approximation to the creation of core holes, we see that the extra-atomic reduction Δ of core-level binding energies, which was written in Eq. (2.2) as a difference of total energy differences, can be written in terms of orbital eigenenergies:

$$\begin{aligned} \Delta \approx & \epsilon_i(\text{chemisorbed atom}; n_i = \frac{1}{2}) \\ & - \epsilon_i(\text{free atom}; n_i = \frac{1}{2}), \end{aligned} \quad (3.5)$$

where i labels the core state from which an electron is removed to the vacuum level. (We have notationally suppressed the fact that Δ depends on i .) Now using first-order perturbation theory

$$\Delta \approx \langle \psi_i | \delta v_{\text{eff}}(\vec{r}) | \psi_i \rangle, \quad (3.6)$$

with

$$\begin{aligned} \delta v_{\text{eff}}(\vec{r}) = & v_{\text{eff}}[n(\vec{r}'; \text{chemisorbed atom} \\ & \text{with } \frac{1}{2} \text{ core hole}); \vec{r}] \\ & - v_{\text{eff}}[n(\vec{r}'; \text{free atom with } \frac{1}{2} \text{ core hole}); \vec{r}]. \end{aligned} \quad (3.7)$$

Here ψ_i is the core-state eigenfunction in either the free or chemisorbed atom with half of a core hole.

The effective potential v_{eff} is the sum of electrostatic and exchange-correlation contributions. The

latter changes very little with changes in the electron density in the core region where $|\psi_i(\vec{r})|^2$ is appreciable. [The exchange and correlation potentials vary with electron density as $n^\alpha(\vec{r})$, where $\alpha \leq \frac{1}{3}$; their derivatives with respect to density therefore go as $n^{\alpha-1}(\vec{r})$, which is very small in the core region.] We can thus neglect the difference between the exchange-correlation components of the two effective potentials in Eq. (3.7) and replace Eq. (3.6) by

$$\Delta \approx \langle \psi_i | \delta \phi(\vec{r}) | \psi_i \rangle, \quad (3.8)$$

where $\delta \phi(\vec{r})$ is the electrostatic component of $\delta v_{\text{eff}}(\vec{r})$. Since the charge distribution that gives rise to $\delta \phi(\vec{r})$ essentially lies well outside the core region, this potential difference shows only a small variation over the extent of the deep core orbitals, and we can replace $\delta \phi(\vec{r})$ in Eq. (3.8) by its value at the origin (position of the adatom nucleus):

$$\Delta \approx \delta \phi(0). \quad (3.9)$$

Now since Δ_c is defined by Eq. (2.4) to be the same type of difference of eigenvalues as Eq. (3.5) (but with the eigenvalues for the systems having no core hole), we can reproduce the above discussion to get the analogue of Eq. (3.9) for Δ_c . We see therefore that the relaxation energy $\Delta_r = \Delta - \Delta_c$ can be written as a difference of two $\delta \phi(0)$'s, one for the case of half a core hole, the other for the case of no excitations. Since we expect that if we were to evaluate the right-hand side of Eq. (3.1) for the case of a half core hole that we would just obtain $\frac{1}{2}n(\vec{r}; \text{extra-atomic})$ to a good approximation (our actual calculations confirm the approximate 10% nonlinearity found by Almladh and von Barth⁷), we can evaluate this difference of $\delta \phi(0)$'s simply as

$$\Delta_r \approx \frac{1}{2} \int \frac{n(\vec{r}; \text{extra-atomic})}{|\vec{r}|} d\vec{r}. \quad (3.10)$$

Thus, the extra-atomic relaxation shift can be approximated by half the electrostatic potential at the position of the nucleus due to the extra-atomic screening charge.

Note that the approximations required to obtain this simple result are even more justified for the differences involved in extra-atomic relaxation than they are for either the free or chemisorbed atom individually. In saying this we have in mind, for example, that the screening due to the contraction of other core orbitals may exhibit some nonlinearity as a function of the fraction of the core hole introduced, but it will be similar in the free and chemisorbed atoms and therefore subtract out of the extra-atomic screening charge. We remind the reader that these approximations were not made in computing the energies displayed in Fig. 2.

The virtues of this approximate formula for the

extra-atomic relaxation energy are that it is simple, direct and readily interpretable. In particular, it allows us to assess the quantitative accuracy of the excited-atom model for the extra-atomic screening charge. The results of using this approximation to the screening charge in Eq. (3.10) are given in column 4 of Table I.⁴⁶ Comparison of these results with those in columns 2 and 3 indicates, as we suggested above, that the excited-atom approximation works well for sodium and silicon, but in chlorine and oxygen, it ignores the effective filling of the p states that would otherwise be available to contain the screening charge.

C. Sensitivity of atom-jellium results

We have described above the results of calculations for four specific systems, characterized by a given substrate density and a specific atom and metal-adatom distance. In this subsection, we discuss briefly the sensitivity of our results to the specifying parameters of the model.⁴⁷

The ability of the excited-atom model to duplicate the results for Δ_r computed for Na and Si using the atom-jellium model indicates that, except in cases where the adatom valence shell is effectively filled and unable to accept the final-state screening charge, the relaxation shift should depend rather little on the substrate. [We have verified this for the case of Si: changing the substrate r_s from two (appropriate to Al) to four (appropriate to Na) while holding the adatom-positive-background separation d fixed,²⁹ changed Δ_r by only 0.3 eV.] In contrast to this insensitivity to the substrate, there is, as seen above, a significant dependence of the relaxation shift on the atomic number of the adatom.

The above-mentioned success of the excited-atom model in conjunction with Eq. (3.10) also indicates that so long as the core state is well localized, relaxation effects do not depend on the principal quantum number of the core level. It should of course be noted that by considering only holes in s levels, we have avoided confronting complexities of multiplet structure and severely nonspherical core electron densities associated with the excitation of other than s electrons from the core.

Just as the relaxation shift is dependent on the adatom atomic number, so also is the chemical shift, as seen in Fig. 2. This latter dependence seems to result chiefly from the fact that the chemical shift is very sensitive to the charge state of the adatom, and the charge transfer is strongly affected by the electronegativity of the adatom (which in turn depends on atomic number). Since the electronegativity of the simple metals does not span a great range, the specific metal substrate

TABLE I. Δ_r is the relaxation (or final-state) shift for deep core levels calculated in the atom-jellium model. $\Delta_r^{(1)}$ is the rather close approximation to Δ_r obtained by evaluating Eq. (3.10) using the calculated extra-atomic screening charge $n(\vec{r}; \text{extra-atomic})$. Evaluation of this equation using the "excited atom" approximation to $n(\vec{r}; \text{extra-atomic})$ gives $\Delta_r^{(2)}$; as discussed in the text, this is only a good approximation when the valence shell of the chemisorbed atom still has "room" to accept the additional screening electron (as in the case of Na and Si). The quantity $\Delta_r^{(3)}$ is itself an approximation to $\Delta_r^{(2)}$ obtained from a table of ionization potentials and affinity levels, as discussed in Ref. 46. This easily computed quantity reproduces the excited-atom result $\Delta_r^{(2)}$ to $\sim \frac{1}{2}$ eV, and thus it too represents a reasonable approximation to the relaxation shift Δ_r when there is "room" in the adatom valence shell.

Adatom	Δ_r (eV)	$\Delta_r^{(1)}$ (eV)	$\Delta_r^{(2)}$ (eV)	$\Delta_r^{(3)}$ (eV)
O(1s)	7.8	7.5	10.1	9.3
Na(2s)	4.5	4.7	4.5	4.3
Si(2s)	5.2	5.5	5.2	5.2
Cl(2s)	4.8	4.9	6.9	6.7

can be expected to be less important in determining the charge transfer contribution to Δ_c than the atomic number of the adatom. (In the fixed-distance calculation for Si mentioned above, Δ_c changed from 1.8 to 1.9 eV when r_s was changed from two to four.)

The chemical shift does in certain cases depend appreciably on metal-adatom separation (we have in mind distance variations of the order of a bohr). We find in the case of a sufficiently high-lying core level (e.g., the 2s level in oxygen), that the level tends to follow the distance dependence of the surface barrier potential much as the valence resonances were seen to follow it in Fig. 3 of Ref. 4. The deep-core-level dependence on distance, however, is a mix of the effects of the surface barrier potential and the variation of charge transfer with metal-adatom separation. (Charge transfer affects the energy of core states more than that of valence states.) Thus, we do not attempt to make any general statement for deep levels.

IV. CONCLUSIONS

Our calculations bear out the fact that the chemical, or initial-state, contribution to the extra-atomic reduction of core-level binding energies depends sensitively on details of the system studied, in particular, the degree of initial-state charge transfer. This is of course consistent with the well established success ESCA (electron spectroscopy for chemical analysis) has enjoyed in correlating core shifts with charge states and chemi-

cal environments. One conclusion (specific to surface studies) is suggested by our calculations: valence resonances and sufficiently high-lying core levels have a more readily interpretable dependence on metal-adatom separation than do the deep core levels.

The relaxation, or final-state, shift seems to be largely independent of details of the metal-adatom system other than the adatom atomic number. Dependence on the principal quantum number of the core level (for deep levels) also appears to be very weak. The simple picture of the screening charge consisting of an electron supplied by the metal, but residing in the valence shell of the excited atom seems quantitatively accurate, so long as the valence shell can accommodate the extra charge. When, as in the case of chlorine, there is insufficient "room" in the valence shell for the screening charge, the environment of the atom can play a somewhat greater role. It is tempting to extrapolate this insensitivity to the point of saying that, so far as relaxation effects are concerned, the metal substrate is usually little more than a structureless reservoir of screening electrons. This is quite fortunate, because it justifies the interpretation of differences in core-level binding energies of a given atom as chemical, or initial-state, effects.¹ A concluding comment about the final-state screening effect concerns the theoretical apparatus required to describe it. Our calculations indicate that the extra-atomic response to the presence of the core hole is essentially linear, but, as the success of the excited-atom model of the screening charge suggests, the dielectric function describing the spatial distribution of this charge must contain the structure of the valence shell of the atom that has the core hole; the response function of the bare metal does not capture the qualitative aspects of the screening.

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APPENDIX: EFFECT OF PERTURBATIONS ON Δ

The energy of a system of electrons of density distribution $n(\vec{r})$ in an external potential $v(\vec{r})$ is shown by Hohenberg and Kohn¹⁷ to be

$$E[n] = \int v(\vec{r})n(\vec{r}) d\vec{r} + F[n], \quad (\text{A1})$$

with $F[n]$ a universal functional independent of v . Consider the first-order energy change due to a change δv in the external potential (which induces a particle-conserving change in density δn):

$$\begin{aligned} \delta E = & \int \frac{\delta E[n]}{\delta n(\vec{r})} \Big|_{\text{const } v} \delta n(\vec{r}) d\vec{r} \\ & + \int \frac{\delta E[n]}{\delta v(\vec{r})} \Big|_{\text{const } n} \delta v(\vec{r}) d\vec{r}. \end{aligned} \quad (\text{A2})$$

Hohenberg and Kohn show that the first term is zero (stationarity of the energy at constant v), so

$$\delta E = \int n(\vec{r}) \delta v(\vec{r}) d\vec{r}; \quad (\text{A3})$$

this is the expected first-order perturbation theory result.

If we consider δv to be the pseudopotential perturbation discussed in the text (i.e., the difference in potential between a lattice of pseudopotentials and the uniform positive background), then combining Eqs. (2.2) and (A3) gives

$$\begin{aligned} \delta \Delta = & - \int \delta v(\vec{r}) [n(\vec{r}; \text{chemisorbed atom} \\ & \text{with core hole}) \\ & - n(\vec{r}; \text{chemisorbed atom})] d\vec{r} - \delta \Phi. \end{aligned} \quad (\text{A4})$$

Here $\delta \Phi$ is the change in work function induced by δv (which has been discussed and evaluated in Ref. 22), and $n(\vec{r}; \text{chemisorbed atom with core hole})$ is the electron density distribution in the metal-adatom system with an additional electron at the Fermi level to compensate for the charge of the core hole.

It might be thought that we could proceed equally well to find an expression for $\delta \Delta$ by using Eq. (3.5) for Δ in terms of the half-occupation eigenvalues. We begin by writing

$$\delta \Delta \approx \delta \epsilon_i(\text{chemisorbed atom}; n_i = \frac{1}{2}). \quad (\text{A5})$$

Let $\delta v_{\text{eff}}(\vec{r})$ be the change in effective potential of the chemisorbed system with half a core hole which occurs when the perturbation $\delta v(\vec{r})$ is introduced. Then using first-order perturbation theory and Eq. (A5),

$$\delta \Delta = \langle \psi_i | \delta v_{\text{eff}}(\vec{r}) | \psi_i \rangle. \quad (\text{A6})$$

Just such an expression was used in the text to derive Eq. (3.10), but in that case the change of effective potential was known exactly by doing two self-consistent calculations and subtracting the results. Here however we do not know this quantity. This fact is exhibited by writing

$$\delta v_{\text{eff}}(\vec{r}) = \delta v_{\text{eff}}(\vec{r}) \Big|_v + \delta v(\vec{r}), \quad (\text{A7})$$

where

$$\delta v_{\text{eff}}(\vec{r})|_v = \int \frac{\delta v_{\text{eff}}[n; \vec{r}]}{\delta n(\vec{r})} \Big|_{\text{const } v} \delta n(\vec{r}) d\vec{r}, \quad (\text{A8})$$

with $\delta n(\vec{r})$ the density change induced by the perturbation $\delta v(\vec{r})$. It is $\delta n(\vec{r})$ that we do not know, and which would be required to evaluate $\delta\Delta$ via Eq. (A6). The two terms of Eq. (A7) correspond to the

two terms of Eq. (A2) if we replace E in the latter equation by ϵ_i . In the case of the total energy E , however, the first term (that involving δn) vanished because of the variational theorem, while no such simplification occurs for the eigenvalues ϵ_i . (We again remind the reader that only an empirical justification has been given for applying the theorems of the density-functional formalism to a system constrained to have a deep core hole.)

- ¹General reviews on this subject include K. Siegbahn *et al.*, *ESCA: Atomic, Molecular, and Solid State Structure by Means of Electron Spectroscopy* (Almqvist and Wiksells, Uppsala, 1967); L. Hedin, *Ark. Fys.* **30**, 231 (1965); D. A. Shirley, *J. Electron Spectrosc.* **5**, 135 (1974); U. Gelius, *Phys. Scrip.* **9**, 133 (1974); D. Menzel, *J. Vac. Sci. Technol.* **12**, 313 (1975); C. R. Brundle, in *Electronic Structure and Reactivity of Metal Surfaces*, edited by E. G. Derouane and A. A. Lucas (Plenum, New York, 1976), p. 389; D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, *Phys. Rev. B* **15**, 544 (1977).
- ²The term extra-atomic has sometimes been used in the past to refer only to effects spatially outside the atom. We do not find this definition helpful in the present discussion.
- ³N. D. Lang and A. R. Williams, *Phys. Rev. Lett.* **34**, 531 (1975).
- ⁴N. D. Lang and A. R. Williams, *Phys. Rev. Lett.* **37**, 212 (1976).
- ⁵Cf. also O. Gunnarsson, H. Hjelmberg, and B. I. Lundqvist, *Phys. Rev. Lett.* **37**, 292 (1976).
- ⁶Cf. also J. R. Smith, S. C. Ying, and W. Kohn, *Phys. Rev. Lett.* **30**, 610 (1973).
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- ⁸A. R. Williams and N. D. Lang (unpublished).
- ⁹J. W. Gadzuk, *Phys. Rev. B* **14**, 2267 (1976). We note in this connection that our calculations describe the fully screened (but not recombined) core hole, so that the Δ SCF excitation energy we compute would correspond, in a photoemission experiment, to the high-kinetic-energy edge. If the ionized atom is coupled sufficiently weakly to the metal and the passage of the screening charge from the metal is therefore very slow, significant spectral weight in the photoemission spectrum may be given to relaxation energies corresponding to an imagelike distribution of screening charge while it is still in the metal, as discussed by Gadzuk and in Refs. 10 and 11.
- ¹⁰G. E. Laramore and W. J. Camp, *Phys. Rev. B* **9**, 3270 (1974).

- ¹¹See also B. Gumhalter and D. M. Newns, *Phys. Lett. A* **57**, 423 (1976).
- ¹²See however the calculation of P. S. Bagus and K. Hermann [*Solid State Commun.* **20**, 5 (1976)] for CO bonded to a Ni atom, which is used to discuss the chemisorption of CO on Ni.
- ¹³We do not consider systems in which core-hole fluctuations are important, such as discussed by G. Wendin, M. Ohno, and S. Lundqvist, *Solid State Commun.* **19**, 165 (1976).
- ¹⁴P. S. Bagus, *Phys. Rev.* **139**, A619 (1965).
- ¹⁵L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 1.
- ¹⁶W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁷P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹⁸W. Kohn, in *Tokyo Summer Lectures in Theoretical Physics, Syokabo, Tokyo*, edited by R. Kubo (Benjamin, New York, 1966), Part 1, p. 73.
- ¹⁹N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1973), Vol. 28, p. 225.
- ²⁰For example, N. Rösch, in *Electrons in Finite and Infinite Structures*, edited by P. Phariseau (Plenum, New York, to be published).
- ²¹See also W. L. Jolly, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 629.
- ²²N. D. Lang and W. Kohn, *Phys. Rev. B* **1**, 4555 (1970); **3**, 1215 (1971).
- ²³The approximation consists in taking the exchange-correlation contribution to v_{eff} equal to $dg_{xc}(n)/dn$ evaluated at $n = n(\vec{r})$ (the local density), where $g_{xc}(n)$ is the exchange-correlation part of the energy density of a homogeneous electron gas of density n . We use the parameterization of this derivative given by L. Hedin and B. I. Lundqvist, *J. Phys. C* **4**, 2064 (1971).
- ²⁴We use a non-spin-polarized local-density approximation. The error that this makes in the energy of the unpaired electron that is left behind when a hole is produced in, e.g., an s core state subtracts out of the extra-atomic difference. The use of this formulation means in addition that the energies we calculate correspond (approximately) to multiplet averages.
- ²⁵For a discussion of the accuracy of the approximation for valence-electron effects, see O. Gunnarsson and

- P. Johansson, *Int. J. Quantum Chem.* **10**, 307 (1976); O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).
- ²⁶The term chemical shift has not always been used in the literature to include all of these effects; we however find it convenient to use it in this way.
- ²⁷In particular, they correspond only crudely to the energy required to excite an electron. The absolute meaning they do have is given in Eq. (3.2) below.
- ²⁸Our jellium substrate is taken to have $r_s = 2$ (recall that $4\pi r_s^3/3 \equiv 1/\bar{n}$, with \bar{n} the mean interior electron number density, equal to the positive background density). This simulates high-density simple metals such as Al ($r_s = 2.07$).
- ²⁹The equilibrium position of the adatoms Si and Na were calculated using the first-order pseudopotential perturbation theory described in Refs. 4, 5, and 22. Adsorption was taken to be at a threefold site on the (111) face of Al. Let us define the distance from positive background edge to adatom nucleus along the surface normal as d . Then this procedure yields $d = 1.6$ bohr for Si (corresponding to an Al-Si bond length $b = 2.6 \text{ \AA}$) and $d = 2.5$ bohr for Na (corresponding to $b = 3.0 \text{ \AA}$). The calculated Na-Al bond length is in very reasonable agreement with the value found by B. A. Hutchins, T. N. Rhodin, and J. E. Demuth [*Surf. Sci.* **54**, 419 (1976)] using LEED (low-energy-electron diffraction) analysis for Na on Al(100) ($2.86 \pm 0.07 \text{ \AA}$). As discussed in Ref. 4, the first-order theory does not appear to yield reliable results for Cl, and so a value for d was found by using Fig. 3 of this paper in conjunction with the photoemission data of J. E. Rowe cited in Ref. 9 of that paper ($d \sim 1.5$ bohr). See the discussion in the text below for the case of oxygen.
- ³⁰As noted above, the fact that we use the non-spin-polarized local-density approximation means that our calculated binding energy reduction Δ refers to binding energies which are differences of (approximately) multiplet-averaged energies of the system (free atom or chemisorbed atom) with and without a core hole. The Δ which we derive from experiment should therefore also refer to multiplet averages if we wish to compare it with this calculated value. Since we expect multiplet effects in the chemisorbed case to be small, this means that the free-atom binding energy which we subtract from the measured value for the chemisorbed system must be a difference of multiplet-averaged energies. We obtain this multiplet-averaged binding energy as follows: References 31 and 32 give the energy difference between oxygen with a 1s hole in the 4P state and oxygen in its ground (3P) state as 544.5 and 543.5 eV, respectively (we express this as 544.0 ± 0.5 eV). Reference 31 gives an energy for the 2D state of the ion (oxygen with 1s hole) which is 4.1 eV higher than that of the 4P state, while Ref. 32 gives an energy for the 2P state of the ion that is 4.43 eV higher than that of the 4P state. If we use Slater's integrals (p. 343 of Ref. 33) to parametrize these results, and use the value 0.54123 Ry (extracted from experiment) given on p. 341 of Ref. 33 for $F^2(2p, 2p)$ in the oxygen atom in its ground state, then we find a multiplet-averaged binding energy (i.e., difference between multiplet-averaged energies for the ion and the atom) of 545.9 ± 0.5 eV.
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- ³³J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I.
- ³⁴C. R. Brundle (private communication) finds a binding energy relative to the Fermi level of 531.8 eV for the 1s state of oxygen at very low coverages on aluminum. (This value does not change by more than ~ 0.2 eV as adsorption proceeds to the point where spectral lines characteristic of the Al in Al_2O_3 are seen.)
- ³⁵We add the work function of the Al(111) surface, found by J. K. Grepstad, P. O. Gartland, and B. J. Slagsvold [*Surf. Sci.* **57**, 348 (1976)] to be 4.24 eV. This differs only slightly from the work function of polycrystalline Al, found by R. M. Eastment and C. H. B. Mee [*J. Phys. F* **3**, 1738 (1973)] to be 4.28 eV. Although the distinction between a polycrystalline Al surface and an Al(111) surface is numerically unimportant, it is convenient when calculating the $\delta\Phi$ part of the pseudopotential correction (see Appendix) to consider a particular crystal face, so as not to have to consider the question of the weighting of the different faces in a polycrystalline average.
- ³⁶K. Y. Yu, J. N. Miller, P. Chye, W. E. Spicer, N. D. Lang, and A. R. Williams, *Phys. Rev. B* **14**, 1446 (1976).
- ³⁷P. H. Dawson, *Surf. Sci.* **57**, 229 (1976).
- ³⁸D. Briggs, *Faraday Disc. Chem. Soc.* **60**, 81 (1975).
- ³⁹N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **155**, 682 (1967).
- ⁴⁰We have verified the statement that the valence p shell in chemisorbed Cl can accommodate essentially no final-state screening charge in the following way. We have computed the extra-atomic screening charge for the case of Cl with $\frac{1}{4}$ of a 2s hole, and scaled this up by a factor of 4. If it were the case that the valence p shell could accommodate some part of the screening charge induced by the hole (even if not all of it), then in this calculation we would expect the size of the kidney-shaped contour (which we identify with charge that cannot be accommodated in the p shell, and which therefore resides in the metal), to decrease from the size it has in the case of an entire core hole. In fact, however, the size remains essentially the same.
- ⁴¹J. B. Pendry (unpublished).
- ⁴²Half the electrostatic potential at the point-charge position due to the purely metallic linear-response screening charge shown at the bottom left-hand side of Fig. 3 (corresponding to the Na distance) is 4.1 eV; that for the charge shown at the bottom right-hand side (corresponding to the Cl distance) is 6.2 eV. In both cases, the screening charge is scaled up to correspond to a unit point charge. These numbers then represent the purely metallic linear-response estimates for Δ_r (see Sec. III B).
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- ⁴⁴J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.
- ⁴⁵A. R. Williams, R. A. deGroot, and C. B. Sommers, *J. Chem. Phys.* **63**, 628 (1975).
- ⁴⁶It is shown by A. R. Williams and N. D. Lang in Ref. 8 that the relaxation shift Δ_r can be approximated by the following combination of measured free-atom quantities: $\Delta_r \approx \frac{1}{2} \left\{ \frac{1}{2} [I_1(Z+1) - A(Z)] + \frac{1}{2} [I_2(Z+1) - I_1(Z)] \right\}$, where $A(Z)$, $I_1(Z)$ and $I_2(Z)$ are, respectively, the elec-

tron affinity and the first two ionization potentials of the free atom with atomic number Z . Reference to the next atom (atomic number $Z+1$) reflects the use of the "equivalent cores" approximation in obtaining this relation. The two expressions within the curly brackets are individually estimates, although somewhat less accurate, of Δ_{ν} ; the first is an underestimate, the second an overestimate. (We have neglected effects of

multiplet averaging in evaluating this formula in Table I, and have used values of A , I_1 , and I_2 that refer to the ground states of the atom and ion.)

⁴⁷We also note here the corrections $\delta\Delta$ (pseudopotential) that were calculated for Na, Si, and Cl at a threefold site on an Al(111) surface at the distances given in Ref. 29. They are -0.2 , -0.5 , and 0.3 eV, respectively.

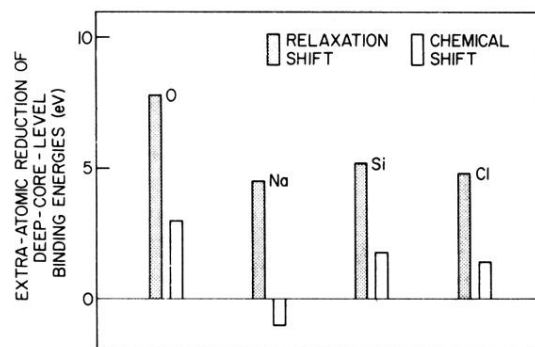


FIG. 2. Decomposition of extra-atomic reduction of deep-core-level binding energy into its two components. Single atoms of O, Na, Si, and Cl chemisorbed on high-density ($r_s = 2$) simple-metal surface. Metal-adsorbent separations for Na, Si, and Cl are given in Ref. 29; oxygen was placed inside the metal (see text). Hole state is $1s$ for O, $2s$ for Na, Si, and Cl.