Core level shifts of rare-gas atoms implanted in the noble metals

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By means of soft-x-ray photoemission Citrin and Hamann have observed core level shifts of Ne, Ar, Kr, and Xe atoms implanted in the noble metals and have constructed a theoretical model with which to interpret the results. We describe calculations employing a quite different approach to the same physical effects which are as successful numerically. The two salient elements are the energy associated with the screening of the core hole by the host-metal electrons and the potential shift arising from the surface dipole of the metal, neither of which is present in the free-atom case. Also considered is the chemical shift due to implantation in the host; estimates of this depend upon details of the model describing the implant site, but for the case at hand we find this contribution to be small.

I. INTRODUCTION

Analysis of the absolute binding energy of a core electron excited in an x-ray photoemission experiment reduces, in first approximation, to assessing the validity of Koopmans' theorem, that is, to investigating the role of correlation effects and the extent to which the remaining electrons screen the final-state hole. Chemical effects are presumably better studied by examining shifts of core level lines in different environments. Perhaps the prototype of this class of experiment is the shift observed between the free-atom case and that of the atom in a solid or molecule, a matter of concern in the original work of Siegbahn and collaborators.[1,2] More recently Ley *et al.*[3] enjoyed some numerical success in analyzing free-atom → metal shifts for simple systems such as Na and Ca, but their scheme works less well for the transition metals.[4] These studies were hampered by the paucity of free-atom experimental information; core level binding energies *measured* for the metals were compared with those *calculated* for the free atoms. For the rare gases atomic data are available. Recently Citrin and Hamann (hereafter referred to as CH) have conducted a careful study[5] of Ne, Ar, Kr, and Xe implanted in the noble metals (with the exception of Kr in Au). CH also constructed a theoretical model which is physically plausible and satisfactorily reproduces the experimental trends. In this paper we describe an alternate scheme to treat the *same* effects which is as reasonable physically, less sensitive to the choice of input parameters, and as successful numerically. We emphasize, however, that the success of a scheme in numerically reproducing experimental data does not necessarily imply an understanding of the mechanisms responsible for the shifts. Our results, alone or in conjunction with the earlier investigations, do not resolve the factors contributing to the chemical shifts; they do help to define the questions which must be addressed and answered prior to any justified claim of understanding of these core level shifts.

The shift ΔE_B of a core level binding energy is defined by

$$\Delta E_B = E_B^0(\text{atom}) - E_B^0(\text{implant})$$
$$= [E(\text{ion}) - E(\text{atom})]^0$$
$$- [E_{\text{final}}(\text{implant}) - E_{\text{initial}}(\text{implant})]^0 ,$$

$$(1)$$

where the superscript 0 indicates that all energies are referred to some *common* zero; the reference-level problem will be discussed shortly. ΔE_B consists of various elements which we loosely separate into a screening contribution and a chemical shift:

(i) *Screening contribution.* The free atom is positively charged after the photoemission event, but in the implanted situation the Fermi sea acts to screen the final-state hole. This response of the medium is termed extra-atomic screening; its extent obviously depends on the medium, but whatever its magnitude it reduces the binding energy of the photoelectron by lowering the total energy of the final implant state. Photoexcitation also leads to a relaxation of the ionized atom's wave functions around the final-state hole. Since a change of environment may modify the electron states of the atom, this intra-atomic screening of the core hole may correspondingly change and thus contribute to the level shift. It

is universally assumed, however, that intra-atomic screening differs insignificantly between the atomic and solid states. This assumption is imposed by computational necessity rather than physical rigor. We make a crude test of this assumption in Sec. V.

(ii) *Chemical shift.* Implantation of the atom necessitates the compression of its outer-electron wave functions. The Coulomb interaction between the outer and core electrons is increased by the compression, and the core-electron binding energy is reduced. In general other chemical effects may be connected with the transition from free atom to solid. There may be changes in valence-state occupancies; for example, the transition metals tend to have larger d and smaller s counts than their free-atom counterparts. In a compound or an alloy, a given atomic site may even be charged.

Equation (1) specifies that the component binding energies of ΔE_B have a common reference energy in order that the shift be independent of any such arbitrary quantity, as CH and others have emphasized. Experimentally, the free-atom binding energy is measured with respect to the vacuum zero, while for the implanted situation the reference is the Fermi level ϵ_F of the photoemission apparatus with which the sample is in contact; ϵ_F differs from the vacuum zero by the work function ϕ of the sample under study. For our theoretical considerations the vacuum zero is the free atom reference. For the implanted case, however, our reference level is the crystal zero, which is the bulk metal analog of the vacuum zero and differs from the latter by the surface dipole term D as defined by Seitz.[6] Put another way, the crystal zero is the electrostatic potential at a point on the boundary of a Wigner-Seitz (WS) cell of a metal; as Bardeen[6a] emphasizes, this reference level gives a zero surface dipole energy if the electron distribution of a WS cell at the surface of a metal were the same as that of an interior cell. We use this reference since our treatment of the implants employs the renormalized atom approach,[9] in which the natural reference level is the crystal zero. Owing to the disparities in reference energies, there are several ways by which theory and experiment may be compared. We adopt the convention of CH and in defining ΔE_B refer all binding energies to the vacuum level:

$$\Delta E_B(\text{expt}) = E_B(\text{atom}) - [E_B(\text{implant}) + \phi] , \quad (2)$$

$$\Delta E_B(\text{theor}) = E_B(\text{atom}) - [E_B(\text{implant}) + D] .$$

The superscript has been deleted; it is to be understood that measured or calculated binding energies have the individual reference levels described above. In particular, the connection between theory and experiment is

$$\Delta E_B(\text{theor}) = \Delta E_B(\text{expt}) + (\phi - D) . \quad (2')$$

CH employed a jellium model of the host metal, introducing a uniform dielectric coincident with the positive background in order to better approximate the polarization response of the filled d bands lying below ϵ_F. Within this model the surface dipole term D was calculated. The implanted rare-gas atom was assumed to occupy a spherical cavity from which the jellium background was excluded. Appropriate pseudopotentials were used to describe the implant in either the initial neutral state or the photoionized situation with a core hole, and the response of the electron gas calculated in each case. CH's estimate of $\Delta E_B(\text{theor})$ thus consists of calculating the surface dipole energy of the host and the polarization response to the initial and final implant pseudopotentials. The difference in polarization energy between the neutral- and ionized-implant cases provides a measure of extra-atomic screening, which is the "polarization shift" in their description; intra-atomic screening effects are not included. CH combined the surface dipole and the neutral-implant polarization energy estimates into an "initial-state potential shift"; in our nomenclature this is the chemical shift *plus* the surface dipole term D. No crystallographic data are available for the inert gases in the noble metals, but nevertheless CH made reasonable estimates of sphere radii (for further discussion see Sec. IV); unfortunately, as they indicate, these choices are not straightforward. We believe there is an uncertainty of at least several tenths of an angstrom in the radii chosen and that CH's results would be significantly affected by changes of this order.

We pursue a different approach to the screening and chemical-shift terms. In regard to extra-atomic screening we follow the scheme of Ley et al.[3] and ask what screening would occur if the screening charge were supplied to the free atom. We rewrite Eqs. (1) and (2) to explicitly exhibit such an extra-atomic screening term Δ_S:

$$\Delta E_B(\text{theor}) = [E(\text{ion}) - E_{\text{final}}(\text{implant})]$$
$$- [E(\text{atom}) - E_{\text{initial}}(\text{implant})] - D$$
$$[E(\text{ion}) - E(\text{ion} + \text{screening electron})]$$
$$+ \delta E - D \equiv \Delta_S + \delta E - D , \quad (3)$$

where the extra-atomic screening term Δ_S is

$$\Delta_S \equiv E(\text{ion}) - E(\text{ion} + \text{screening electron}) \quad (4)$$

and the "chemical-shift" term δE is

$$\delta E \equiv [E_{\text{initial}}(\text{implant}) - E_{\text{final}}(\text{implant})]$$
$$- [E(\text{atom}) - E(\text{ion} + \text{screening electron})] . \quad (5)$$

If we assume that the screening energy Δ_S calculated for the free atom represents a good approximation for the extra-atomic screening *in the implanted case*, δE becomes

$$\delta E = [E_{\text{initial}}(\text{implant}) - E_{\text{final}}(\text{implant},$$

$$\text{without screening})] - [E(\text{atom}) - E(\text{ion})] ; \quad (5')$$

this version is used in the calculations to be described. The procedure we use to calculate the free-atom screening energy Δ_S is more rigorous than that employed by Ley *et al.* Section II describes our computation of Δ_S in addition to comparing calculated free-atom binding energies with experiment. Δ_S alone quite satisfactorily reproduces the variation in the free-atom → given-noble-metal-host level shift for the different rare gases.

Short of a direct calculation of the host-metal Fermi level with respect to the potential zero, i.e., a calculation of $\phi - D$, one cannot avoid an estimate of the surface dipole term D. In Sec. III, D is estimated with the method of Lang and Kohn.[7] While d dielectric terms are neglected, we believe the results to be numerically superior to those of CH.[8] Section IV compares $\Delta_S - D$ with the measured shifts; the combination of the two terms provides as good numerical agreement with experiment as the results of CH. Investigation of δE, which encompasses the chemical shift and any change of intra-atomic screening, is deferred until Sec. V. Within the renormalized-atom approach,[9] δE is very crudely estimated with and without the inclusion of intra-atomic screening. The calculations suggest that δE is small for the inert-gas atoms.

II. FREE-ATOM CALCULATIONS: BINDING ENERGIES AND SCREENING ESTIMATES

As a preliminary to our estimate of extra-atomic screening we compare free-atom calculations with the measured gas-phase binding energies. Relativistic Hartree-Fock calculations[10] were performed for the free rare-gas atoms and for the ions with appropriate core holes.[11] Table I summarizes the results; experimental values are from the studies[12] of Johansson *et al.* The

TABLE I. Free-atom binding energies of inert-gas core electrons (all values in eV).

Level	E_B(expt)	E_B(calc)	$|\epsilon|$
Ne $1s$	870.4	869.6	893
Ar $2p_{3/2}$	248.6	248.1	260
Kr $3p_{3/2}$	214.6	217.1	226
Xe $3d_{5/2}$	676.4	676.5	695

one-electron eigenvalues ϵ, which do not include final-state relaxation or correlation effects, yield binding energies larger than either experiment or the difference between the initial- and final-state total energies:

$$E_B^{\text{calc}}(\text{atom}) = E(\text{ion}) - E(\text{atom}) . \quad (6)$$

The intra-atomic screening energy is defined by

$$\Delta_I = |\epsilon| - E_B^{\text{calc}}(\text{atom}) \quad (7)$$

and is roughly 10 eV for the Ar $2p_{3/2}$ and Kr $3p_{3/2}$ holes and about 20 eV for the Ne $1s$ and Xe $3d_{5/2}$. On this scale $E_B^{\text{calc}}(\text{atom})$ agrees with the measurements since the largest discrepancy is 2.5 eV for Kr; correlation contributions are evidently small for these levels. No simple trend in $E_B^{\text{expt}}(\text{atom}) - E_B^{\text{calc}}(\text{atom})$ can be discerned, although inspection of the limited data available for other inert-gas levels suggests that this quantity is similar for core electrons having the same n, l, j quantum numbers; for example, $E_B^{\text{calc}}(\text{atom})$ is smaller than the observed binding energy for both the Ne and Ar $2p_{3/2}$ states.

We estimate extra-atomic screening for the free-atom situation. Specifically, we calculate the total energy of the final-state ion with the core hole and the total energy of an excited atom with the same hole plus an outer screening electron; the difference between the two provides an estimate of the extra-atomic screening energy:

$$\Delta_S = E(\text{ion}) - E(\text{ion} + \text{screening electron}) . \quad (4)$$

We emphasize that a complete Hartree-Fock calculation is carried out in each case. Alternatively Ley *et al.*[3] combine the "polarization-potential" and "equivalent-core" schemes to obtain

$$\Delta_S = \tfrac{1}{2}[F^0(\text{hole, screening electron})$$

$$+ \text{exchange terms}] . \quad (8)$$

Here F^0 is a Slater integral representing the Coulomb interaction between the core orbital excited on photoemission and a screening electron whose wave function is calculated for a neutral atom with Z greater by 1 than that of the photo-excited atom, thus crudely accounting for the ionicity of the final state. Equation (4) is as easy to compute as Eq. (8) and is superior to Eq. (8) in at least two ways. It involves the element in question, not an adjacent one. More importantly, it allows for the possibility that the screening charge may overlap the valence electrons already present. If this occurs, the valence electrons relax and more effectively shield the screening charge so that

$$\Delta_S \lesssim |\epsilon(\text{screening electron})| . \quad (9)$$

Here ϵ is the one-electron energy of the screening electron. This effect is included by performing a

TABLE II. Conduction–electron screening Δ_S as estimated by free–atom calculations.

Inert gas	Δ_S (eV)
Ne	4.8
Ar	4.0
Kr	3.8
Xe	3.5

self-consistent atomic calculation for the configuration having both a core hole and a screening electron, as stipulated in Eq. (4). For core state photoexcitation in a polyvalent atom or transition metal, valence-electron relaxation substantially reduces the bare screening effect. For the problem at hand the screening charge resides well outside the closed outer shells of the inert-gas atoms and

$$\Delta_S \sim \left| \epsilon(\text{screening electron}) \right| . \tag{10}$$

Calculations with screening electrons of varying l indicate not surprisingly that s electrons are most effective for the inert gases. Results for s-electron screening are given in Table II. Δ_S represents the screening energy by which the core level binding is reduced when the s electron is delivered to the free ion from infinity. This is "total" screening in the sense that the ion has been made electrically neutral. CH apparently find screening terms of the same order as those of Table II.

III. SURFACE DIPOLE LAYER

We require values for the surface dipole term D of the noble metals. For this purpose we appeal to Lang and Kohn's electron-gas calculations,[7] the principal aim of which is prediction of the work function ϕ. Lang and Kohn obtain results which are in good accord with experiment for the simple and polyvalent metals; for the noble metals they find $\phi \gtrsim 3.5$ eV whereas the measured work functions[13] for Cu, Ag, and Au are 4.3–4.8, 4.0–4.4, and 4.7–5.2 eV, respectively. The range of experimental values stems from the different experimental techniques and varying sample characteristics such as surface condition. Despite the neglect[14] of the d bands (which are not far below ϵ_F) in the theory, agreement with experiment is fair.

Lang and Kohn's estimate of ϕ is divided into a dipole term, $\Delta\phi$ in their notation, and an ϵ_F term. Unfortunately for our purposes, their reference level is not the crystal zero but the average internal potential sampled by the electron gas; this is the natural reference for such calculations and is used by CH as well. In order to identify the dipole term as defined by Seitz, Lang

and Kohn[15] employed Ashcroft pseudopotentials[16] of the form

$$V_{\text{pseudo}}(r) = \begin{cases} -Z/r , & r \geq r_c \\ 0 , & r < r_c \end{cases} \tag{11}$$

where Z is the effective ionic charge and r_c the ion core radius. Assuming uniform electron density throughout the Wigner-Seitz sphere (of radius r_{WS}) they found the change ΔD in the dipole term resulting from the change in reference energy to be

$$\Delta D = -\frac{3}{10} \frac{Z}{r_{\text{WS}}} \left[1 - 5 \left(\frac{r_c}{r_{\text{WS}}} \right)^2 \right] . \tag{12}$$

Alternatively, assuming that the conduction electrons are excluded from the core region, we find

$$\Delta D = -\frac{3}{10} \frac{Z}{r_{\text{WS}}} \frac{1 - 5(r_c/r_{\text{WS}})^2 + 5(r_c/r_{\text{WS}})^3 - (r_c/r_{\text{WS}})^5}{[1 - (r_c/r_{\text{WS}})^3]^2} . \tag{13}$$

The second choice is more appealing on physical grounds but the first is more consistent with the other elements of Lang and Kohn's calculations. Values of D both with respect to the average potential and relative to the crystal zero [through use of Eqs. (12) and (13)] are given in Table III; Ashcroft and Langreth's Z and r_c values[16] have been used. The work of CH suggests that d-electron dielectric screening effects may enhance these terms by ~10% for Ag and as much as ~25% for Cu and Au. We must emphasize that CH properly dealt with this reference-level problem by always taking differences between energy terms calculated relative to a common energy reference (in their case, the average internal potential).

Judging in part from the range of the entries in Table III, it appears that the uncertainty in D is greater than the uncertainty[17] in ϕ; in what follows we will use D values based on Eq. (13). The dipole terms so obtained are significantly smaller than those tabulated by CH; this stems *principally* from our use of Lang and Kohn's analysis and results, though also from the different choice of reference energy. In the case of Cu, for ex-

TABLE III. Surface dipole energies D (eV).

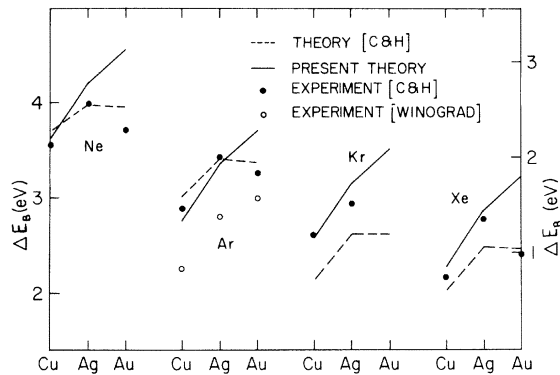| Metal	D (relative to average potential)	D (relative to crystal zero) Eq. (12)	D (relative to crystal zero) Eq. (13)
Cu	3.4	1.6	1.2
Ag	2.4	1.2	0.6
Au	2.3	0.6	0.3

FIG. 1. Core level shifts ΔE_B of rare-gas atoms implanted in Cu, Ag, and Au. Measured shifts are given by the filled circles (Citrin and Hamann) and the open circles (Kim and Winograd). The dashed lines are the theoretical results of Citrin and Hamann, and the solid lines the calculations of this paper. The energy scale on the right is for the theoretical values obtained by Citrin and Hamann; all other points are referred to the scale on the left.

ample, CH obtain $D = 5.9$ eV (Table III of Ref. 5) relative to the average internal potential; this is to be compared with Lang and Kohn's value of 3.4 eV relative to the *same* reference level (see Table III of this paper).

CH's potential energy (or initial state) shift (Fig. 3 of Ref. 5) represents the difference in energy between the metal-vacuum surface dipole and the dipole induced at the implant site by the response of the host electron gas to the neutral implant pseudopotential. Their potential shift cannot be directly compared with our D of Table III since, in our nomenclature, their initial state shift also includes a chemical shift component.

IV. COMPARISON WITH EXPERIMENT

We momentarily ignore the chemical effects subsumed into δE of Eq. (3) and compare the experimental data with what has been calculated to this point. Figure 1 displays the shifts measured by CH:

$$\Delta E_B(\text{expt}) = E_B(\text{atom}) - [E_B(\text{metal}) + \phi] . \qquad (2)$$

As indicated before, the work function has been introduced so that both implanted- and free-atom binding energies are referred to the vacuum zero. The observed free-atom binding energies $E_B(\text{atom})$ are taken from Ref. 12 (see Table I). CH assumed Eastman's photoemission work-function values,[13] which are 4.65, 4.0, and 5.1 eV for Cu, Ag, and Au, respectively. With this choice their data feature a peak in ΔE_B at silver. This may derive from their use of a work function for Ag which is at the lower end of the gen-

erally accepted values (see Sec. III), while that for Au is at the upper end. If the work functions of the measured samples were used, $\Delta E_B(\text{expt})$ might well increase monotonically from copper to gold. Kim and Winograd have made independent measurements[18] for argon in these hosts. Their results, incorporating the same ϕ and $E_B(\text{atom})$ values, are also presented in Fig. 1; they lie slightly outside CH's stated experimental uncertainties for Cu and Ag and within for Au.

Neglecting δE, our estimates are given by

$$\Delta E_B(\text{theor}) = \Delta_S - D , \qquad (14)$$

in which Eq. (13) has been used in computing D; these are displayed in the figure, as are CH's theoretical values, which have been uniformly shifted upward by 1.40 eV (the mean deviation of their calculated results from the observed shifts). We note that the Δ_S term of Eq. (14) depends *only* on the gas atom and D *only* on the host metal. In conjunction the two terms compare quite favorably with $\Delta E_B(\text{expt})$. For a given host, the variation within inert gas is tracked rather well, while for a given implant, the change from host to host is less satisfactorily described (assuming that uncertainties in the work functions have not masked the trend). Use of Eq. (12) instead of Eq. (13) in the estimate of D lowers our curves by approximately 0.5 eV without significantly altering their shape. It is tempting to assert that the purely atomic aspect of the screening, our Δ_S, provides an explanation of the trend from one inert gas to another; however, the results of CH also agree reasonably with experiment. Numerical agreement with experiment does not necessarily imply the uniqueness of the model describing these processes.

It is useful in this context to point out how sensitive the placement of the bands with respect to the crystal zero is to the method used to construct the potential. For Ni, self-consistent calculations [20] (within the framework of the renormalized atom scheme) have been done for two different potentials: one is of the Hartree-Fock-Wigner-Seitz type and the other uses the local density approximation for exchange and correlation after the manner of Hedin and Lundqvist. In the latter case the Fermi level relative to the crystal zero is nearly 5 eV higher. In the language of this paper this means that $(\phi-D)$ has been shifted by 5 eV depending on what method is used to construct the potential. Accordingly one must be somewhat restrained in claiming agreement between theory and experiment since $(\phi-D)$ plays such a crucial role [see Eq. (2')] as we discussed in the Introduction.

TABLE IV. Difference δE_{sp}, Eq. (16), between free and renormalized core level one-electron energies and the radii R of the atomic spheres.

Level	Cu host		Ag and Au hosts	
	δE_{sp} (eV)	R (Å)	δE_{sp} (eV)	R (Å)
Ne $1s$	0.3	1.81	0.2	1.91
Ar $2p_{3/2}$	0.6	2.09	0.5	2.17
Kr $3p_{3/2}$	0.8	2.18	0.6	2.29
Xe $3d_{5/2}$	1.2	2.30	0.9	2.40

V. CHEMICAL SHIFT AND INTRA-ATOMIC SCREENING

Our ΔE_B estimates of Sec. IV included only a free-atom approximation for the extra-atomic screening contribution. In this section we consider the chemical shift and change of intra-atomic screening associated with insertion of the inert-gas atom into the host-metal matrix; these effects constitute the δE term of Eq. (3). The principal factor involved is the distortion of the outer electron wave functions of the inert gas (the $2s$ and $2p$ shells of neon, for example) by the host environment, plus any charging of the inert-gas site. To gain some sense of the scale of these effects we crudely describe this distortion through the use of simple renormalized-atom[9] ideas.

Crucial to our estimate is the model of the implant site, specifically the radius of the sphere containing the rare-gas implant. No crystallographic data exist for the inert gases in the noble metals, although some information[19] is available for alkali-metal impurities. CH attributed the effective volume per alkali atom, in the dilute limit, to the rare-gas atom adjacent in the Periodic Table. It was further noted that each implant sphere radius so obtained is roughly equal to the inert-gas van der Waals radius and that the two scale together from row to row in the Periodic Table. This lent plausibility to the volumes chosen and suggested an extrapolation scheme for the cases where pertinent alkali–noble-metal alloy data are unavailable. These radii are listed in Table IV; as emphasized by CH, these would appear to be underestimates since the inert-gas atoms are undoubtedly more repulsive than their alkali neighbors. Predictions are significantly affected if these radii were to be changed by several tenths of an angstrom.

CH represented the implanted atoms by pseudopotentials defined within spheres having these radii and calculated the response of the host electron gas. We look at the problem differently by focusing attention on the implant rather than the host. A measure of chemical effects due to implantation can be obtained by asking what is the impact on the atom *if the implant sphere is taken*

to be electrically neutral. This is a reasonable choice for an implant in a metallic environment if the size of the implant sphere has been well chosen. By truncating the rare-gas orbitals at the radius R of the atomic sphere and normalizing them to unity within the sphere we can make both single-particle and total energy difference estimates of δE.

We represent the initial implant state by a rare gas atom "renormalized" to the implant sphere; the surrounding electrons of the host are assumed to retain their WS cell charge distribution. The unscreened implant site specified in Eq. (5′) is represented by a "renormalized" ion having the appropriate core hole. Equation (5′) becomes

$$\delta E = [E_{ren}(\text{atom}) - E_{ren}(\text{ion})] - [E(\text{atom}) - E(\text{ion})] .$$
$$(15)$$

The total renormalized energies E_{ren} are not good variational quantities since they do not result from self-consistent calculations with suitable boundary conditions imposed within the atomic sphere; nonetheless, they may be used for rough estimates.

A. Single-particle estimate

In the single-particle picture the bracketed terms of Eq. (15) are approximated by one-electron energies, so that

$$\delta E_{sp} = \epsilon_{ren}(\text{core electron}) - \epsilon_{free}(\text{core electron}) .$$
$$(16)$$

Under the assumption of charge neutrality, the single-particle prediction for the chemical shift is thus simply given by the difference between the free and renormalized one-electron energies of the excited core level. Table IV lists the values we have calculated. In addition to the chemical shift, Eq. (15) for δE provides a crude estimate of any change of intra-atomic screening, whereas δE_{sp}, given by Eq. (16), does not. On the other hand, δE_{sp} is much less susceptible to numerical errors introduced by the crude description of the valence-electron charge. Moreover, we know that δE_{sp}, as calculated, overestimates the chemical shift. Consider, for example, an atom whose valence electrons become the conduction bands or the covalent bonding orbitals in the solid. Simple renormalization of the free-atom valence orbitals overcompresses the valence charge since bonding in either a metal or covalent material involves charge buildup between ion cores, that is, in the outer regions of the atomic sphere. It is to be noted, however, that the renormalization shifts of Table IV are smaller than those for atoms such as C (covalent) or Fe (metallic); since the outer s and p shells of the rare gases are presumably more corelike than bonding, the tendency of δE_{sp} to overestimate the shifts is probably somewhat less

as well.

Let us consider the implications of taking the δE_{sp} values of Table IV at face value, that is, identifying δE_{sp} as a good approximation to the chemical shift and incorporating it in Eq. (3) for ΔE_B. Our theoretical curves of Fig. 1 then move upwards by an amount δE_{sp}. The increase is 0.3 eV for Ne, rising to 1.2 eV for Xe. This makes ΔE_B(calc) roughly the same for all the implants, no longer reproducing the experimental trend. The change in one-electron energy, however, is extremely sensitive to the sphere radius, as comparison of the δE_{sp} values for Cu with those for the other hosts demonstrates.

We may contrast these results with those of CH. CH's potential energy shift (Fig. 3 of Ref. 5) ranges from -1.8 to -2.8 eV; the initial state shift in our model is $(\delta E_{sp} - D)$, which ranges from 0.9 to $+0.6$ eV.[21] The disparity is due primarily to the larger metal-vacuum dipole energies estimated by CH (see Sec. III). By excluding the surface dipole term from the initial state shifts in both models we may also compare what we identify as the chemical shifts; namely, we may compare δE_{sp}, the chemical shift in our model, with CH's initial state shift excluding the surface dipole energy (care must be taken to compare the results relative to a common reference). We find CH's chemical shifts to be generally larger than those in our work. It is difficult to compare our and CH's treatment of the implant site. We impose charge neutrality of the sphere ascribed to the implant site. CH's model consists of a pseudopotential within a spherical cavity in jellium; the resulting charge shift into the cavity produces a "cavity dipole." We estimate[22] a charge of about one electron within their cavity (with, of course, an equivalent amount of positive charge outside). Nieminen[23] has treated the same model within the density functional approach without making the Weizsäcker approximation for the kinetic energy and found a decreased charge but, more importantly, a less diffuse charge density and hence a smaller "cavity dipole." Consequently, we believe CH's larger chemical shifts may be due to excessive negative charging of the implant site. On the other hand, whatever error CH may make in calculating the charge density inside the implant site is probably roughly compensated (as they indicate) by a similar error in computing the charge shift at the metal-vacuum surface. The resulting calculation of $(\phi - D)$, used in Eq. (2'), may then be less sensitive, than one would guess, to their treatment of the implant site.

B. Total energy estimate

The total energy difference estimate of the chemical shift and change of intra-atomic screen-

ing is simply obtained by evaluating Eq. (15). We find

$$\delta E \lesssim 0.1 \text{ eV} . \tag{17}$$

The inequality holds even for radii as much as 1–2 a.u. smaller than those of Table IV. This result is at least an order of magnitude smaller than the single-particle estimate and, if taken seriously, leads to the following inference: If the renormalization shift of the core level one-electron energy δE_{sp} is interpreted as an increase in the energy of the initial implant state relative to the free-atom case, then the very small value of δE given by the inequality (18) means that intra-atomic screening of the photoionized implant state must correspondingly *decrease*. Unfortunately, unlike the case for δE_{sp}, we do not know the sign of the error in δE. Nevertheless, trusting our calculations which indicate intra-atomic screening changes in the direction implied by the inequality (18), we find that the intra-atomic screening is inhibited as valence charge is compressed into the atomic cell on implantation.

VI. DISCUSSION

The analysis of the core level shifts presented here differs from that of CH in the imposition of charge neutrality on the implant sphere and in the estimate, albeit crude, of the intra-atomic screening component of the shift; with the exception of the intra-atomic contribution, however, both schemes deal with the same physical effects. Although our results agree somewhat better with experiment, both theoretical procedures encompass rather drastic simplifying assumptions, and neither can be unambiguously asserted to be unique. The theory of such processes is still at a primitive level; quantitative prediction of core-state shifts even for systems as apparently elementary as those treated here still represents an intriguing problem which requires further investigation. Perhaps distinctions among the various physical effects would be easier to discern if similar experiments were performed with alkali-metal hosts.

We emphasize that the experimental and theoretical results of CH and our calculations all demonstrate that the shifts vary principally with the implanted species and that changes with host are appreciably smaller. Kim and Winograd[18] have reached the opposite conclusion from the data of CH. We believe the similarities in the electronic structure of the three noble metals are primarily responsible for the greater dependency of the shifts upon implant rather than host.

Finally, the conclusion which emerges from the work is that more ambitious treatments of similar experiments for such complicated systems as atoms and molecules adsorbed on surfaces

should be treated with skepticism.

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[22]The amount of charge may be ascertained by integration of CH's electron density profile for Ne in Cu (Fig. 2 of Ref. 5), which yields $-1|e|$.

[23]We are indebted to Risto Nieminen (NORDITA, Copenhagen) for performing these calculations. Incidentally, for the case of the neon-sized cavity in Cu with no pseudopotential he recovers the Lang-Kohn value of 3.4 eV which they obtained for the metal-vacuum surface dipole.