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Theory of Auger relaxation energies in metals

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A theory of the Auger parameter ξ is introduced and used to interpret measurements on the $3d$ transition metals. This parameter is the combination of an Auger energy and related core-level binding energies which formally eliminates the contributions of chemical shifts and reference levels, permitting the unambiguous extraction of a relaxation energy from measured quantities. The value of ξ is the result of two competing effects which cancel approximately in some cases, but not in others. This leads to an interesting variation of ξ with atomic number. Our parameter-free calculations describe both the magnitude of this quantity and its strong increase at the end of the transition series, where the character of the screening charge changes from d-like to s-like.

I. INTRODUCTION

In a recent paper[1] we used the atom-jellium model, developed for the study of atomic chemisorption on simple metals,[2] to study in detail the static aspects of the metallic screening of holes created in deeply bound core levels. The study provided direct theoretical support for a particular model of the metallic screening process for which the previous support had been primarily empirical. In this model, the metal plays the limited role of a structureless source of screening charge; the spatial distribution of the screening charge and hence its effect on core-level spectra is governed by the valence states of the ionized atom.[1,3–5] A subsequent study[6] of these binding energies in $3d$ transition metals confirmed the utility of this simple "excited-atom" model of metallic screening.

The measurement considered in Ref. 6 is the change in the binding energy of core electrons which accompanies the condensation of free atoms to form a metal. The analysis of this binding-energy shift is complicated by several factors. First, experimental data for the free atoms used as a reference are unavailable for transition elements. Second, the binding-energy shift results not only from screening effects, but depends as well on other differences between the free atom and the solid (the surface dipole-layer potential, the compression of the free atom into the volume it occupies in the solid, and changes in the distribution of valence electrons among s, p, and d states). In this paper we apply the theoretical methods developed in Ref. 6 to a measured quantity which unambiguously focuses on screening effects, and which, our analysis indicates, is amenable to a very simple physical interpretation that is supported by existing measurements.

The Auger parameter ξ which we wish to consider is the following combination of core-level binding energies ω_l and the Auger energy ω_{ijk}:

$$\xi \equiv (\omega_i - \omega_j - \omega_k) - \omega_{ijk} , \tag{1.1}$$

where each of the ω's can in turn be expressed as a total-energy difference. Such an energy parameter was considered earlier by, e.g., Yin, Tsang, and Adler.[7] It shares the advantages of Wagner's[8] Auger parameter α (defined as $\omega_{ijk} - \omega_l$, where l need not equal i, j, or k) but is somewhat more convenient for theoretical discussion, since all of the large core-level binding energies are subtracted out. In terms of the total energy $E(n_j)$ of the entire solid considered as a function of the occupation of, e.g., the jth level (spin orbital) of a particular atom, the binding energy of an electron in this level is given by

$$\omega_j = E(0) - E(1) . \tag{1.2}$$

Using the same notation, the Auger energy in terms of the total energy $E(n_i, n_j, n_k)$ considered as a function of the occupations of the ith, jth, and kth levels of the same atom is

$$\omega_{ijk} = E(0,1,1) - E(1,0,0) . \tag{1.3}$$

That is, the Auger energy ω_{ijk} is the total energy released when an electron in the jth level of a particular atom drops into a (previously created) hole in the ith level and an electron is ejected to vacuum from the kth level. Note that, as defined in Eqs. (1.2) and (1.3), the ω's are all positive quantities.

If the definitions of the ω's [Eqs. (1.2) and (1.3)] are substituted into the definition of ξ [Eq. (1.1)], then we see that ξ is formally equivalent to the change in the binding energy of the jth electron caused by removing the kth electron; i.e.,

$$\xi \equiv \omega_j^{(k)} - \omega_j , \tag{1.4}$$

where $\omega_j^{(k)}$ is the binding energy of the jth electron in the presence of a hole in the *k*th level; i.e., in terms of total energies $E(n_j,n_k)$,

$$\omega_j^{(k)} \equiv E(0,0) - E(1,0) \ . \tag{1.5}$$

We see in this way that ξ is completely independent of the properties of the *i*th atomic level. Since we expect that removing an electron (the *k*th) will make all other electrons (in particular the *j*th) more tightly bound, we conclude from Eq. (1.4) that in general $\xi > 0$. It is also immediately clear from Eq. (1.4) that ξ is purely a relaxation effect, by which we mean that, in the language of Ref. 6 or of Fermi-liquid theory, ξ involves no terms which are of order lower than two in occupation-number changes. Each of the binding energies ω_j and $\omega_j^{(k)}$ appearing in Eq. (1.4) is a first-order quantity (a total-energy difference or equivalently an excitation energy). In contrast to the ω's, the Auger parameter ξ is the change in the first-order quantity ω_j corresponding to a change in occupation; it therefore contains no first-order contributions. The physical implications of this mathematical distinction are that the quantity ξ is obscured by neither chemical shifts nor reference energies, both of which affect first-order quantities.

We continue the analysis by taking the total energies contributing to ξ [through Eqs. (1.2) and (1.5)] to be analytic functions of n_j and n_k, the number of electrons in the *j*th and *k*th atomic levels. Doing this allows us to expand the total energy differences of interest in Taylor series in the relevant occupation-number changes, e.g.,

$$E(n_j+\delta n_j) - E(n_j) = \frac{\partial E}{\partial n_j}\delta n_j + \frac{1}{2}\frac{\partial^2 E}{\partial n_j^2}(\delta n_j)^2 + \cdots \ . \tag{1.6}$$

The convergence of such series for the case in which $|\delta n_j| = 1$ has been studied by Slater.[9] Now it has been formally demonstrated by Janak[10] that within the density-functional formalism,[11-14]

$$\frac{\partial E}{\partial n_j} = \epsilon_j \ , \tag{1.7}$$

where ϵ_j is the orbital eigenenergy appearing in the Schrödinger-like equation of the Kohn-Sham self-consistent-field method.[12] Thus, for example

$$\omega_j \equiv E(0) - E(1) = -\epsilon_j + \frac{1}{2}\frac{\partial \epsilon_j}{\partial n_j} + \cdots \ . \tag{1.8}$$

This relationship between the binding energy ω_j and the orbital eigenenergy ϵ_j, together with the expression for the Auger parameter ξ in terms of binding energies [Eq. (1.4)], makes it clear that to leading order ξ is given simply by

$$\xi = \frac{\partial \epsilon_j}{\partial n_k} \ . \tag{1.9}$$

Our analysis of the Auger parameter ξ up to this point is equally valid for free atoms and solids. For the study of free atoms, Eq. (1.9) is all that is required. That is, self-consistent-field calculations can be carried out for several occupations of the *k*th atomic level; the variation of the *j*th atomic level with n_k then gives ξ according to Eq. (1.9).[15]

Calculations based on Eq. (1.9) for solids are unfortunately far more difficult. Even without the complications introduced by the presence of core holes, an energy-band calculation would be required. The removal of core electrons from particular atoms in the crystal destroys the translational invariance on which energy-band theory is based, making the calculation of core levels such as ϵ_j and their variation with n_k vastly more difficult yet. It is in order to avoid this compounded difficulty that we use the excited-atom model[1,6,16] of the metallic screening process.

Equation (1.9) indicates that the quantity of interest is the variation of the *j*th core level as charge is removed from the *k*th core level. In a solid, the removal of charge from the *k*th level is accompanied by the arrival of screening charge which preserves local neutrality. The variation of the *j*th core level of the solid ϵ_j^S during such a process is simulated in the excited-atom model by the variation of the *j*th level of the free atom ϵ_j^A as charge is "excited" from the *k*th level to the lowest empty valence level, i.e.,

$$\epsilon_j^S(n_k-\delta) - \epsilon_j^S(n_k) \approx \epsilon_j^A(n_k-\delta, n_v+\delta) - \epsilon_j^A(n_k,n_v) \ , \tag{1.10}$$

where the second argument of ϵ_j^A is the occupation of the valence level. (This equation states simply that the effect of the screening charge on the core levels of the metal is similar to the effect of additional valence charge on the core levels of a free atom—see Refs. 1 and 6.) Substituting this approximation to the n_k dependence of ϵ_j^S into our expression for the Auger parameter ξ [Eq. (1.9)], we obtain

$$\xi^S \approx \frac{\partial \epsilon_j^A}{\partial n_k} - \frac{\partial \epsilon_j^A}{\partial n_v} \ , \tag{1.11}$$

where, once again, we use the superscripts *S* and *A* to distinguish between quantities appropriate to the solid and to the free atom. As with Eq. (1.9), Eq. (1.11) is correct to leading order (second) in occupation-number changes; terms of the next order (third) are accounted for by evaluating Eqs. (1.9) and (1.11) at $n_j = n_k = \frac{1}{2}$. The valence occupation number n_v is set to preserve charge neutrality, as prescribed by the model[17]: $n_v = n_v^0 + 1$, where n_v^0 is the occupation in the free unexcited atom. (While the labels *j* and *k* refer to individual spin orbitals, implying that $n_j = 1$ and $n_k = 1$ correspond to full occupation, the label v refers to all of the valence states taken together, and so in general n_v will be greater than unity.) This method of including next-to-leading-order terms is entirely analogous to the analysis used in Ref. 6 and that leading to Slater's transition-state concept.[9]

Equation (1.11) is our basic result and one of its implications is immediate. This equation tells us that the Auger parameter ξ represents the effect on the jth level of moving charge from the kth level to a valence level, and this implies that ξ will be small when the levels corresponding to k and v belong to the same principal-quantum-number shell. Since the electron distributions associated with different states belonging to a given principal-quantum-number shell are all concentrated in a common annular region surrounding the nucleus, and since the annular regions corresponding to different principal-quantum-number shells are almost mutually exclusive, the electrostatic effects of transferring charge between different shells are much larger than those caused by transfers within the same shell. Thus, for example, we expect on the basis of Eq. (1.11) that ξ for the LMM transition (initial state—hole in $n=2$ shell; final state—two holes in $n=3$ shell) in the first transition-metal series will increase sharply with increasing atomic number as the metallic screening charge changes in character from $3d$ to $4s$ with the filling of the d band at the end of the series.

II. RESULTS AND COMPARISON WITH EXPERIMENT

We evaluate ξ for the case just mentioned, an LMM core Auger line for solid metals in the first transition series, from K to Zn. We would like to avoid the complications of multiplet structure as much as possible and so we do not consider the case $LM_{23}M_{23}$ (final state—two $3p$ holes); but on the other hand the seemingly ideal case[18] LM_1M_1 (final state—two $3s$ holes) corresponds to lines that are too weak to permit the assembling of sufficient data for comparison with experiment. The remaining possibility is LM_1M_{23}; we choose the particular case $L_3M_1M_{23}(^3P)$ (initial state—$2p_{3/2}$ hole; final state—one $3s$ hole and one $3p$ hole, in relative triplet state).[18]

Even for this case there is very little experimental data; we use values that were obtained by Davis and Shirley.[19] To calculate the derivatives in Eq. (1.11), we solve the density-functional equations of Kohn and Sham[12,13] self-consistently for the atom of interest, with the relevant orbital occupation numbers, and extract the derivatives numerically by performing the evaluations at two closely spaced values of n_k and of n_v. We solve the equations in their spin-polarized form,[13] using the local-density approximation for exchange and correlation.[14,20] Our assumption of spherical symmetry for the free atom means that the Schrödinger-like equation of the Kohn-Sham method reduces to a one-dimensional radial differential equation, which we solve numerically. The particular choice of valence state to simulate the metallic screening charge[21] is discussed below and in the Appendix.

Figure 1 gives our results; we note again that our theory has no adjustable parameters. The substantial increase in ξ which we associate with filling of the d shell at the end of the series is seen in both the theory and the experiment.[19,22] The data are consistent with the argument made above that ξ is an intrinsically positive quantity. We can only speculate that the rapid variation among the transition metals seen in the experimental data (if confirmed by further measurements) might be related to magnetic effects not included in our analysis.

As an aside, we note that results of this type are often presented by giving a table comparing experimental Auger energies with "theoretical" (or "semiempirical") Auger energies obtained by combining a calculated Auger parameter ξ with measured core-level binding energies (i.e., $\omega_{ijk}=\omega_i-\omega_j-\omega_k-\xi$). Thus for Sc, e.g., the experimental $L_3M_1M_{23}(^3P)$ Auger energy (referred to the Fermi level[19]) is 319.0 eV, while our value for this quantity is 318.4 eV. This form of presentation does not however make the fractional error involved in the theory as apparent.

To provide an independent measure of the accuracy of our treatment of ξ, we calculate ξ for the $L_3M_1M_{23}(^3P)$ Auger line in an Ar atom, and compare this in Table I with the experimental value.[23] We include, in addition, data for the $KL_1L_{23}(^3P)$ line

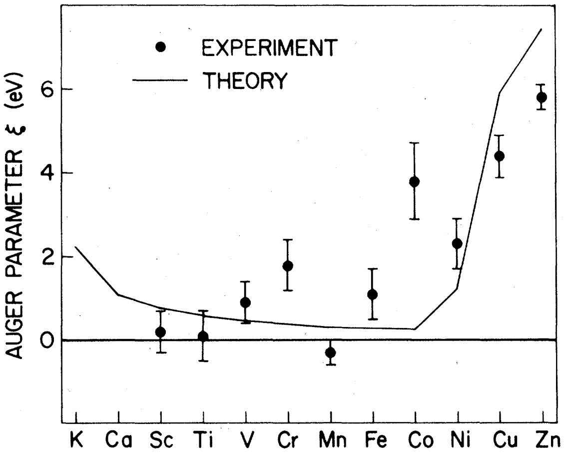

FIG. 1. Comparison of calculated values of the Auger parameter ξ for the $3d$ transition series with experimental values (see Ref. 19). The Auger line considered is $L_3M_1M_{23}(^3P)$. Error bars reflect only the uncertainty in the values of the Auger energy, and not the core-level binding energies.

TABLE I. Comparison of measured and calculated values of ξ for two free atoms, and two metals outside the series given in Fig. 1. In the calculation for the metals, $\partial/\partial n_v$ was taken to be $\partial/\partial n_s$, and not $\partial/\partial n_p$, as discussed in the text.

Case	ξ_{expt} (eV)	ξ_{theory} (eV)
Ar atom $(L_3M_1M_{23}{}^3P)$	12.7[a]	12.4
Ne atom $(KL_1L_{23}{}^3P)$	18.2[a]	19.5
Na metal $(KL_1L_{23}{}^3P)$	10.1[b]	11.3
Mg metal $(KL_1L_{23}{}^3P)$	10.4[b]	12.4

[a] See Ref. 23.
[b] See Ref. 26.

in Ne.[23] [Note in this connection that the experimental results for the atoms can be checked by evaluating Eq. (1.4) directly using atomic outer-shell optical data.[24] The values obtained in this way differ from those in Table I (obtained from inner-shell Auger data and core-level binding energies) by $\lesssim 0.2$ eV.]

Our calculation gives $\xi(L_3M_1M_{23}{}^3P)$ for Ar correctly to 0.3 eV. This suggests that in the $3d$ series (which has an Ar core and in which we consider the same Auger line), our treatment gives an accurate value for the "intra-atomic" part of ξ.[25]

The error in Ne for $\xi(KL_1L_{23}{}^3P)$ is larger (1.3 eV) than the error noted for Ar. This suggests that, for this line and core structure, the local-density approximation used in our calculations is not as accurate, and that such an error would be present if we were to study the $KL_1L_{23}({}^3P)$ line in metals with the Ne core. The results given for Na and Mg metal[26] in Table I are consistent with this expectation. Note, however, that the calculated screening ("extra-atomic") contribution to ξ given by the excited-atom approximation is also uncertain by a similar amount (see below).

We have argued above that the intra-atomic aspects of our calculations for the $3d$ transition metals possess an accuracy more like that of our result for free atomic Ar than that of the result for free atomic Ne. Consistent with this argument is the fact that the Auger parameter ξ for the transition metals cannot be significantly smaller than our calculated values without violating the requirement that $\xi > 0$.

III. DISCUSSION OF THE EXCITED-ATOM MODEL

One of the basic points of our three studies of core-hole relaxation effects (the present work and Refs. 1 and 6) is that the excited-atom model of the metallic screening of core holes provides an effective way of simplifying an otherwise very complicated problem. We discuss below our understanding of the limitations of this model.

Now one of the most important virtues of the model is that it distinguishes between those cases in which the screening electron penetrates and perturbs the ionized atom, and those cases in which the screening electron is forced to reside "outside" the ionized atom. One reason that we call attention to this particular aspect of the model is that it is in this regard that it differs most strongly from the other commonly used model of core-hole screening, that of simple dielectric-response theory.[27] Since relaxation effects involve in a basic way the electrostatic effect of the screening charge on the core,[28] the distribution of the screening charge is particularly important in cases where the screening electron can penetrate the ionized atom. This is the case for transition metals, where the screening charge is accommodated in the open d shell.[29] To determine the character of the screening charge in the transition series, we combined the results of self-consistent energy band calculations with the equivalent-core concept.[30] The band calculations show that the number of d electrons increases by almost exactly unity as we move from each metal to the next in the $3d$ transition series. Now in the equivalent-core approximation, the presence of a core hole in an atom of atomic number Z transforms its valence aspects into those of the atom of atomic number $Z+1$. Applying this notion locally in a transition metal thus suggests simply that a core hole is screened by the addition of a d electron. This combination of the band-calculation results with the equivalent-core concept worked very well in our analysis of core-level binding-energy shifts,[6] but this represents only empirical evidence for its validity.

In sharp contrast to the situation in transition metals is the case of rare-gas atoms implanted in metals. Because the valence shell of the rare-gas atom is filled, the screening charge is forced to remain outside the atom. This exclusion of the screening charge can also be seen in our study of the core holes in chemisorbed chlorine.[1] Because the $3p$ shell of Cl fills as part of the chemisorption process, it behaves like a rare-gas atom in not accepting additional charge when a core hole is introduced.

One might expect that the proper use of the model for such systems would amount to introducing the screening charge into the next (empty) principal-quantum-number shell, e.g., the 4*s* level in the case of implanted Ar. However, limited evidence suggests that the physical picture implicit in such use of the model is not completely correct. This evidence is contained in our studies of chemisorbed alkali atoms. According to the equivalent-core concept, a rare-gas atom containing a core hole that has been screened by contact with a metal is similar to an alkali atom (in contact with the metal). Alkali atoms are very electropositive and tend to lose their outermost valence electron to the metal, as seen in our study of chemisorption.[2] The valence electron of the alkali is very similar to the screening electron of the rare gas with a core hole, and so the fact that the alkalis tend to give up this electron suggests that the screening electron in the case of rare-gas atoms is not best thought of as residing in orbitals of the atom, but rather as residing in the metal. The excited-atom model therefore does not seem to contain the essential physics of metallic screening for these systems. The model has however given numerically successful results for rare gases embedded in metallic foils.[3] The resolution of this apparent paradox can be seen in the contour plots of the electron density associated with alkali chemisorption (see Fig. 3 of Ref. 2), which show that, although the alkali valence level loses its electron to the metal, metallic screening results in a screening-charge distribution residing at an average distance from the ionized atom that is similar to the average distance of charge in the atomic orbital. Since core-level relaxation energies depend only on this average distance, the excited-atom model provides a reasonable estimate of relaxation energies even though the physical picture it embodies is not entirely correct. We should not lose sight of the fact that, even in such cases, the model does contain the physical aspect of greatest quantitative importance—the exclusion of the screening charge from the interior of the ionized atom. The volume excluded in this way varies from one rare-gas implant to the next and is responsible for the observed[31,32] variation of the screening energy. A recent study of relaxation energies for rare-gas implants by Waclawski, Gadzuk, and Herbst[31] synthesizes the excited-atom and dielectric-response models of screening, using the former to justify a rigid exclusion of the screening charge from the interior of the atom and the latter to approximate its distribution outside the atom.

The discussion above deals with the limiting cases in which the screening charge resides either inside or outside the ionized atom, the prototypes being transition metals and rare-gas implants in metals. We consider now the intermediate case of simple (and noble) metals. These metals constitute an intermediate case because the screening charge is partially inside the atomic cell and partially outside. This situation raises several questions with regard to the excited-atom model. First, the screening charge is almost certainly not dominated by states of a single angular-momentum character; the question arises of whether we should, for example, try to estimate the contribution of *p*-like (in addition to *s*-like) electrons. Second, the fact that the Thomas-Fermi screening length is smaller than the Wigner-Seitz radius of these sytems suggests that neutrality is maintained in each atomic cell, which in turn suggests that the screening charge is compressed into the cell in much the same way that the free-atom electron density is compressed into the neutral atomic cells of the metallic ground state.[33] We have estimated these effects and found them both to be approximately 1 eV in magnitude, with the compression effect somewhat larger for Cu and Zn than for Na and Mg.

Compression and *p* admixture act in opposite directions on the magnitude of the Auger parameter. While it might be possible to elaborate the excited-atom model to account for these effects, we have adopted a view that is consistent with our understanding of the rare-gas implant case, namely, that these effects are fundamentally beyond the scope of the simple model. We have chose, therefore, to retain its simplicity by ignoring compression effects and by taking the screening charge to have *s* character[34] whenever it is not confined to the interior of the atom (as it is for transition metals).

We can summarize the above discussion as follows. The excited-atom model of core-hole screening is most appropriate when the screening charge can be accommodated inside the ionized atom, as in the transition metals. This is fortunate because the screening energy is largest in this case and also because the model accurately describes the large perturbation of the other valence states by the screening charge. When the screening charge resides in the outermost valence shell, as in simple metals, the model oversimplifies the portion of the screening-charge distribution residing outside the atomic cell. When it resides outside the atom entirely, as in rare-gas implants, the physical picture implied by the model is probably incorrect. Nonetheless, for both simple metals and rare-gas implants, by correctly describing the volume close to the atomic core from which the screening charge is excluded by orthogonality requirements, the model provides screening-energy estimates of sufficient accuracy for many purposes.

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APPENDIX: CHARACTER OF THE VALENCE SCREENING CHARGE

In using the excited-atom model to discuss the Auger parameter ξ, we wish to think about the free atom for the case in which there are between 0 and 2 core holes, which would imply the presence of between 0 and 2 additional (screening) electrons in the valence shell. For the case of no core holes, we want the electronic configuration of the atom (the distribution of electrons among *s*, *p*, and *d* subshells) to be similar to that which the atom has in the unexcited solid.[35] For Ca through Cu, the configurations were taken to be $3d^{n+0.6}4s^{1.4}$ with n running from 0 to 9; for K and Zn they were $3d^04s^1$ and $3d^{10}4s^2$, respectively. These, to within 0.1 electron, are the configurations obtained in a band calculation,[36] with all fourth-shell (non-*d*-like) valence electrons taken to be *s*-like. Using the equivalent-core approximation[30] indicates that the appropriate configurations for the two-core-hole case are $3d^{n+0.6}4s^{1.4}$ with $n=1$ for K through $n=9$ for Co; and $3d^{10}4s^24p^m$ with $m=0$ for Ni through $m=2$ for Zn.[37] As discussed in the text, the derivative $\partial/\partial n_v$ in these cases was always taken to be a derivative with respect to *s* occupation, and not *p* occupation.

Now note that in the range from 0 to 2 core holes, the character of the screening charge changes (between *d* and *s*-*p*) for the cases of Ni, Cu, and K, which corresponds to a discontinuity in $\partial\epsilon_j^A/\partial n_v$.[38] This fact turns out to make a power-series formulation of ξ of the type discussed in the text very cumbersome to use for these cases; it is much more convenient to proceed in the following way.

We use Eq. (1.7) and integrate by parts to obtain

$$E^S(0,n_k)-E^S(1,n_k)=\int_1^0 \epsilon_j^S(n_j,n_k)\,dn_j=-\epsilon_j^S(1,n_k)+\int_0^1 n_j\,\frac{\partial\epsilon_j^S(n_j,n_k)}{\partial n_j}\,dn_j\;. \tag{A1}$$

Then, from Eq. (1.4), we have

$$\begin{aligned}\xi&=[E^S(0,0)-E^S(1,0)]-[E^S(0,1)-E^S(1,1)]\\&=\int_0^1\frac{\partial\epsilon_j^S(1,n_k)}{\partial n_k}\,dn_k+\int_0^1 n_j\left[\frac{\partial\epsilon_j^S(n_j,0)}{\partial n_j}-\frac{\partial\epsilon_j^S(n_j,1)}{\partial n_j}\right]dn_j\;.\end{aligned} \tag{A2}$$

The excited-atom model in the form of Eq. (1.10) can be used to express derivatives of $\epsilon_j^S(n_j,n_k)$ in terms of derivatives of $\epsilon_j^A(n_j,n_k,n_v)$

$$\frac{\partial\epsilon_j^S}{\partial n_k}=\frac{\partial\epsilon_j^A}{\partial n_k}-\frac{\partial\epsilon_j^A}{\partial n_v}\;, \tag{A3}$$

and a similar equation with $\partial/\partial n_k$ replaced by $\partial/\partial n_j$. The atomic valence occupation number is set to preserve charge neutrality, as prescribed by the model: $n_v=n_v^0+(1-n_j)+(1-n_k)$, with n_v^0 the valence occupation in the free unexcited atom (in the solid configuration). Within the context of the excited-atom approximation, therefore, Eq. (A2) becomes

$$\begin{aligned}\xi=&\int_0^1\left[\frac{\partial\epsilon_j^A(1,n_k,n_v^0+1-n_k)}{\partial n_k}-\frac{\partial\epsilon_j^A(1,n_k,n_v^0+1-n_k)}{\partial n_v}\right]dn_k\\&+\int_0^1 n_j\left[\left[\frac{\partial\epsilon_j^A(n_j,0,n_v^0+2-n_j)}{\partial n_j}-\frac{\partial\epsilon_j^A(n_j,0,n_v^0+2-n_j)}{\partial n_v}\right]\right.\\&\qquad\left.-\left[\frac{\partial\epsilon_j^A(n_j,1,n_v^0+1-n_j)}{\partial n_j}-\frac{\partial\epsilon_j^A(n_j,1,n_v^0+1-n_j)}{\partial n_v}\right]\right]dn_j\;.\end{aligned} \tag{A4}$$

The ranges of integration here were divided into segments in which the screening charge maintained a given character,[39] and the midpoint rule was used to evaluate the integral over each segment.

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[14] We remind the reader that the theorems of the density-functional formalism have been proven just for the ground state of the system, and that there is only an empirical justification (see, e.g., Ref. 6) for applying the formalism to cases in which there are deep core holes.

[15] Terms of the next order in the Taylor series are included by evaluating the derivative at the appropriate fractional occupation numbers (see below).

[16] This model was used to study Auger spectra by S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B 8, 2387 (1973). See also, R. Hoogewijs, L. Fiermans, and J. Vennik, Surf. Sci. 69, 273 (1977); F. P. Larkins, Chem. Phys. Lett. 55, 335 (1978); At. Data Nucl. Data Tables 20, 311 (1977).

[17] The excited-atom model of metallic screening implies the rigid maintenance of neutrality. The occupation numbers used in Ref. 6 to estimate the contribution of metallic screening to the binding-energy *shift* which accompanies metal formation correspond to a non-neutral system because the shift represents the *difference* between the metal which preserves local neutrality, and the free-atom reference which does not.

[18] We note here two points concerning the use in this case of the spin-polarized local-density approximation (see Ref. 13) for exchange and correlation. The first is that this approximation will be more accurate for two holes in different subshells (e.g., $3s$ and $3p$ as here) than for two holes in the same subshell (e.g., both in $3s$) because of the greater importance of correlation effects in the latter instance. The second point is that the approximation would not be suitable to treat the $LM_1M_{23}(^1P)$ case because the spin density in such a (Hartree-like) calculation for an atom with holes in different subshells is not zero everywhere in space (though its integral is zero), whereas in fact the spin density is expected to be zero everywhere.

[19] R. F. Davis and D. A. Shirley (private communication) have very kindly obtained for us values of the Auger energies by analyzing existing data from their laboratory, which had not been taken in a way designed to obtain these energies well. For this reason, the error bars given should be considered to be "probable" errors. The binding energies are given in D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, Phys. Rev. B 15, 544 (1977) (0.43 eV should be subtracted from the values for Cr).

[20] The explicit form of this approximation that we use is given in V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978), pp. 15–16.

[21] The electronic charge attracted to the region of the ionized atom is taken to consist of equal numbers of spin-up and spin-down electrons; i.e., the derivative $\partial\epsilon_j^A/\partial n_v$ appearing in Eq. (1.11) is taken to be

$$\frac{\partial\epsilon_j^A}{\partial n_v}=\frac{1}{2}\left[\frac{\partial\epsilon_j^A}{\partial n_v^{\uparrow}}+\frac{\partial\epsilon_j^A}{\partial n_v^{\downarrow}}\right],$$

where $n_v^{\uparrow}$ and $n_v^{\downarrow}$ are the numbers of spin-up and spin-down valence electrons. We also take $n_v^{\uparrow}=n_v^{\downarrow}$, thereby ignoring the effects of magnetic order. All the calculations involved are fully spin-polarized and, in particular, the spin-up and spin-down electron densities are not assumed to be the same. A measure of the importance of spin polarization to the intra-atomic aspects of this problem is the singlet-triplet splitting of the LM_1M_{23} Auger line, which for the $3d$ transition metals is typically ~ 10 eV.

[22] We mention two other sources of data for the Auger line studied here, for Cu and Zn: G. Schön, J. Electron Spect. 1, 377 (1972/73) (data given yield $\xi=2.5$ eV for Cu); J.-M. Mariot and G. Dufour, Chem. Phys. Lett. 50, 218 (1977) (data given yield $\xi=4.8$ eV for Zn).

[23] Binding energies for Ne and Ar from compilation of D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, Ref. 19; Auger energy for Ne from D. L. Matthews, B. M. Johnson, J. J. Mackey, L. E. Smith, W. Hodge, and C. F. Moore, Phys. Rev. A 10, 1177 (1974); Auger energy for Ar from W. Mehlhorn and D. Stalherm, Z. Phys. 217, 294 (1968).

[24] C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. (U.S.) Spec. Publ. (U.S. GPO, Washington, D.C., 1949), Vol. 1.

[25] This would be defined explicitly as the first term in Eq. (1.11) evaluated not at $n_v=n_v^0+1$ but at $n_v=n_v^0$.

[26] Na: A. Barrie and F. J. Street, J. Electron Spect. 7, 1 (1975). Mg: J. C. Fuggle, L. M. Watson, D. J. Fabian, and S. Affrossman, J. Phys. F 5, 375 (1975).

[27] E.g., L. Hedin, Ark. Fys. 30, 231 (1965); J. W. Gadzuk, Phys. Rev. B 14, 2267 (1976).

[28] In the simple case of the core-level binding energy, for example, the relaxation energy is, to lowest order, half of the electrostatic potential in the core region due to the screening charge [see L. Hedin and S. Lundqvist, Solid State Phys. 23, 1 (1969) or Ref. 1].

[29] The effect on the other electrons in the d shell is also substantial. This requires that the screening charge be introduced self-consistently, as emphasized by Watson *et al.* in Ref. 4.

[30] E.g., D. A. Shirley, Chem. Phys. Lett. 16, 220 (1972);

C.-O. Almbladh and U. von Barth, Phys. Rev. B 13, 3307 (1976).

[31] B. J. Waclawski, J. W. Gadzuk, and J. F. Herbst, Phys. Rev. Lett. 41, 583 (1978).

[32] P. H. Citrin and D. R. Hamann, Phys. Rev. B 10, 4948 (1974).

[33] C. D. Gelatt, Jr., H. Ehrenreich, and R. E. Watson, Phys. Rev. B 15, 1613 (1977).

[34] We take $\partial/\partial n_v$ to be a derivative with respect to s occupation; but we still take the configuration about which this derivative is evaluated to be that given by the equivalent-core concept.

[35] Cf. also Ref. 6 and K. S. Kim, S. W. Gaarenstroom, and N. Winograd, Phys. Rev. B 14, 2281 (1976).

[36] See results in Ref. 6. These self-consistent band calculations employed a formalism described by J. Kübler, A. R. Williams, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979). They provide a simple and unambiguous angular-momentum decomposition of the electron density through the use of the spherical (Wigner-Seitz) approximation to the polyhedral atomic cell. In this approximation, the wave function is everywhere represented by products of spherical harmonics and radial functions, the squares of which provide the l decomposition.

[37] Cf. D. R. Jennison, H. H. Madden, and D. M. Zehner (unpublished).

[38] In Ref. 6, the superscript A was used to denote an atom in its actual configuration and A^* to denote one in the solid configuration. In the present paper, since we only consider atoms in their solid configurations, we simply use a superscript A to denote the corresponding quantities.

[39] A rigid-band picture indicates that as the number of core holes is raised, the number of valence s electrons for K first increases to 1.4 (the value for the rest of the transition series) and then the d band starts to fill. For Ni and Cu, it indicates that the d band fills first, and then the valence s-p count starts to increase (from 1.4). This mode of valence-shell filling was used in evaluating Eq. (A4).