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Analysis of Auger-parameter and XPS shifts: Application of potential models

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The use of free-atom-to-metal Auger-parameter shifts to determine atomic-potential parameters for Na, Mg, and Zn is shown to lead to an apparent inconsistency between the effects of perfect screening and the influence of valence-wave-function compression in the metallic state. This conflict is traced to the neglect in standard potential models of the quadratic dependence of the atomic-core potential on valence charge. We propose a generalized model which gives a good description of the atomic-core potential, and show that this can be used to derive empirical solid-state potential parameters from metal-atom Auger-parameter shifts.

I. INTRODUCTION

It is well established that experimental probes of the atomic-core potential, such as chemical shifts in core level binding energies[1,2] and in the Auger parameter,[3–6] offer useful insight into local electronic structure. Chemical shifts have both initial- and final-state contributions, reflecting differences in charge state and relaxation energies.

Potential models in which the core potential V of an atom is assumed to vary linearly with the valence charge q have long been used to analyze chemical shifts.[1,2] Recently, Thomas and Weightman[7] have developed a method of analyzing Auger-parameter shifts that is dependent on model parameters that can be obtained from atomic-structure calculations, with a correction for the compression of the valence wave functions in solids. While this approach is particularly suitable for the determination of charge transfer in alloys,[7–9] its accuracy is limited by the uncertainty in determining the solid-state parameters.

In the present work we study metal-to-free-atom chemical shifts in order to determine solid-state potential parameters empirically for the elements Na, Mg, and Zn. We focus on Auger-parameter shifts since the Auger parameter is a second-order quantity[10] and so has the advantage of not involving the work function and surface dipole of solids required in the analysis of x-ray photoemission spectroscopy (XPS) chemical shifts. Furthermore, the measurement of Auger parameters is determined by peak separations in electron spectra which leads to a cancellation in experimental referencing errors. We find that an analysis of the metal-atom Auger-parameter shifts for these elements within the formalism of Thomas and Weightman[7] leads to an inconsistency between the effects of valence wave-function compression and extra-atomic screening in the metal. A detailed study of the core potential of the Xe atom enables us to trace this apparent contradiction to the neglect of the quadratic dependence of the core potential on valence charge in standard potential models. We propose a generalized model, that gives a good description of the atomic-core potential, and show that this can be used to derive solid-state parameters from metal-atom Auger-parameter shifts.

II. AUGER PARAMETER ANALYSIS

Lang and Williams[10] have defined a general Auger parameter ξ as

$$\xi(jk) = E_k(ijk) + E_b(j) + E_b(k) - E_b(i), \tag{1}$$

where E_k is the Auger kinetic energy and E_b are binding energies. For ijj Auger transitions, Eq. (1) can be written

$$\begin{aligned} \xi(jj) &= 2E_b(j) - E_b(jj) && \text{(2a)}\\ &= E_b(j) - E_b^*(j) && \text{(2b)}\\ &= \mathcal{F}(jj) - R_s, && \text{(2c)} \end{aligned}$$

where $\mathcal{F}$ is the Coulomb repulsion of the two final-state holes, R_s is the static relaxation energy,[11] and $E_b^*(j)$ is the binding energy of the jth core level in the presence of a spectator j hole.

Expanding the binding energies in Eq. (2) as a Taylor series about the ground state, Thomas[12] has shown that $\xi(jj)$ may be expressed in terms of the derivatives of V_j, the potential experienced by an electron in level j, with respect to occupancy N_j:

$$\xi(jj) = \left(\frac{\partial V_j}{\partial N_j}\right)_{N_j=0} - \left(\frac{\partial^2 V_j}{\partial N_j^2}\right)_{N_j=0} + \frac{1}{12}\left(\frac{\partial^3 V_j}{\partial N_j^3}\right)_{N_j=0} - \cdots . \tag{3}$$

More precisely, we define $N = -H$ where H is the number of core holes, and hence the $N_j = 0$ subscripts in Eq. (3) indicate evaluation of the derivatives at the ground-state core configuration. In this notation, $N = -1$ and -2 correspond to singly and doubly core ionized states, respectively.

The contribution to the potential in the atomic core arising from the nucleus and core electrons is chemically invariant to a good approximation, and so potential shifts may be written

$$\Delta V = \Delta V^{\mathrm{valence}} + \Delta V^{\mathrm{ea}}, \qquad (4)$$

where V^{valence} is the contribution to V due to the valence charge density ρ, and V^{ea} is the extra-atomic term. According to classical electrostatics, V^{valence} is given by

$$V^{\mathrm{valence}} = \int \frac{\rho(r)}{r} dr = kq, \qquad (5)$$

where $k \approx 1/r_v$ (reciprocal of the valence shell radius), and q is in units of e. This expression has been used extensively in the analysis of XPS shifts.[1,2,13] More rigorously, k may be defined as the derivative of the core potential with respect to valence charge, and can be evaluated as the change in core eigenvalue upon valence ionization.[7] Substituting $V^{\mathrm{valence}} = kq$ into Eq. (3) and assuming k and V^{ea} vary linearly with N (Ref. 12) gives the Thomas-Weightman[7] expression for Auger parameter shifts:

$$\Delta\xi = \Delta \left\{ q\frac{dk}{dN} + \frac{dq}{dN}\left(k - 2\frac{dk}{dN}\right) + \frac{dV^{\mathrm{ea}}}{dN} \right\}. \qquad (6)$$

It is well known that the compression of the valence wave functions within the Wigner-Seitz cell of a solid increases $\langle 1/r_v \rangle$, and hence $k_{\mathrm{solid}} = \gamma k$ with $\gamma > 1$.[7,14,15] γ may be estimated by comparing $\langle 1/r_v \rangle$ for the atomic wave function with its value for a renormalized valence wave function truncated at the Wigner-Seitz radius, as suggested by Watson and co-workers.[14,15] Following this method, Thomas and Weightman[7] have calculated solid-state parameters $k_{\mathrm{TW}} = \gamma_{\mathrm{TW}} k$ where

$$\gamma_{\mathrm{TW}} = \frac{\langle 1/r_v \rangle_{\mathrm{atomic}}}{\langle 1/r_v \rangle_{\mathrm{renormalized}}}, \qquad (7)$$

and demonstrated that k_{TW} is an upper bound for k_{solid}. Since γ_{TW} is typically ~ 1.3 for simple metals,[16] this procedure for determining k_{solid} is relatively imprecise, giving an uncertainty typically of the order of 15%. Since the atomic parameters are calculated with high accuracy, the uncertainty in γ is the limit of the accuracy to which the solid-state parameters can be obtained.

III. METAL-ATOM AUGER-PARAMETER SHIFTS

For Auger-parameter shifts between metals and free atoms Eq. (6) takes the form

$$\xi_{\mathrm{metal}} - \xi_{\mathrm{atom}} = q\frac{dk}{dN}(\gamma - 1) + \gamma \left[k - 2\frac{dk}{dN} \right] \left(\frac{dq}{dN} \right)_{\mathrm{metal}}. \qquad (8)$$

For free atoms the core hole screening charge dq/dN is necessarily zero, while the assumption of perfect local screening for metallic systems implies $dq/dN = 1$. Since k and dk/dN can be accurately calculated, experimental values of $(\xi_{\mathrm{metal}} - \xi_{\mathrm{atom}})$ can be inserted into Eq. (8) to determine γ empirically. For Mg, $\xi^{\mathrm{Mg}}_{\mathrm{metal}} = 18.2 \pm 0.3$ eV (Refs. 17 and 18) and $\xi^{\mathrm{Mg}}_{\mathrm{atom}} = 28.8 \pm 0.2$ eV,[19–21] giving a metal-to-atom Auger-parameter shift of 10.6 ± 0.4 eV, while $q = -2$ for both phases. Taking[7] $k = 8.8$ eV and $dk/dN = -3.5$ eV, we obtain $\gamma = 0.77$, corresponding to a substantial reduction of k in the solid state which is clearly unphysical. If we impose $1 < \gamma < \gamma_{\mathrm{TW}}$ on Eq. (8) we obtain $15.8 < \xi^{\mathrm{Mg}}_{\mathrm{metal}} - \xi^{\mathrm{Mg}}_{\mathrm{atom}} < 22.4$ eV, in very poor agreement with experiment. Equation (8) can only be made consistent both with the experimental metal-to-atom Auger-parameter shift and with the constraint $\gamma > 1.0$ if dq/dN is reduced to 0.67 which contradicts the assumption of perfect local screening. Similar results were obtained for Zn and Na and we conclude that the formulation of Thomas and Weightman[7] with a potential model of the form $V^{\mathrm{valence}}(N, q) = kq$, with k linear in N and independent of q, does not give a good description of metal-to-atom Auger-parameter shifts.

Given the widespread use of this potential model in XPS and Auger-parameter shift analysis, the origin of the observed contradiction should be traced if reliable determinations of charge transfer are to be deduced from experimental probes of the core potential. To resolve this issue we have carried out a thorough investigation of the core potential V_j of Xe as a function of (i) the core level j, (ii) the valence configuration, and (iii) the number of core holes. Xe was chosen for its large number of core levels and valence electrons.

IV. THE CORE POTENTIAL OF ATOMIC XENON

Figure 1 shows the results for k evaluated as the eigenvalue shift of level nl between the neutral atom and the valence ionized ion[7] as a function of the number of nl core holes using the Dirac-Fock (DF) code of Desclaux.[22] For

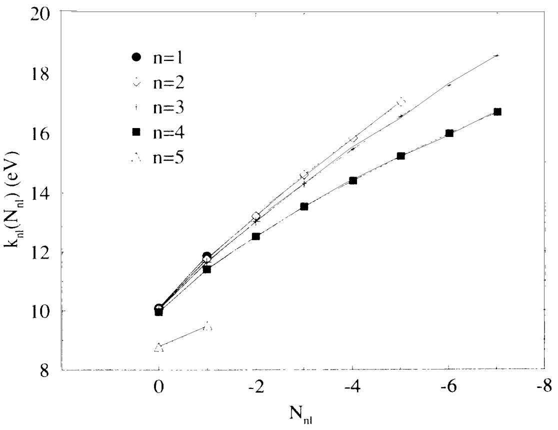

FIG. 1. k_{nl} for Xe evaluated as the nl eigenvalue difference between neutral and valence-ionized "atoms." For each principle quantum shell n, k_{nl} is plotted as a function of N_{nl}, the occupancy of the nl subshell.

a given core configuration, k_{nl} decreases with the principal quantum number n of the core level. For $n = 5$ core and valence orbitals are in the same principal quantum shell and the large overlap of the Xe $5s$ and $5p$ levels gives rise to a substantial reduction of k_{5s}. This effect is also responsible for the observation of smaller XPS chemical shifts for shallow than for deep core levels.[23] Figure 1 also shows slight curvature in $k(N_{nl})$ vs N_{nl}. The linear assumption used in the derivation of Eq. (8) (Ref. 7) is observed to be quite good in the physically relevant region $0 > N > -2$.

The idea that k varies with charge state has been developed by Snyder.[24] This is a quite fundamental question analogous to the transferability of Pauling electronegativity between different states of chemical hybridization. V_{3d} and k_{3d} evaluated as the derivative of V_{3d} with respect to q for Xe are shown in Fig. 2 as functions of valence configuration. We find a quadratic dependence of the potential on q, and hence k increases linearly with valence ionization. An analysis of molecular charge distributions by Saethre, Siggel, and Thomas[25] has also suggested this conclusion. Calculations for a number of core hole states are shown in Fig. 3, and show the gradient of k against q varies slightly with N.

These results may be summarized by writing V^{valence} in the form

$$V^{\text{valence}}(N_{nl}, q) = \int_0^q k(N_{nl}, q')dq', \tag{9}$$

where

$$k(N_{nl}, q) = a + bN_{nl} + cN_{nl}^2 + (d + eN_{nl})q. \tag{10}$$

Numerically fitting the calculated $k^{\text{Xe}}(N_{3d}, q)$ to a polynomial of this form where the ground-state $5s^2 5p^6$ configuration is taken as $q = -8$ we obtained

$$k = 17.69 - 1.21N - 0.04N^2 + (1.00 + 0.03N)q, \tag{11}$$

while a second fit imposing $c = e = 0$ over a smaller range gave

$$k = 17.69 - 1.27N + 0.98q. \tag{12}$$

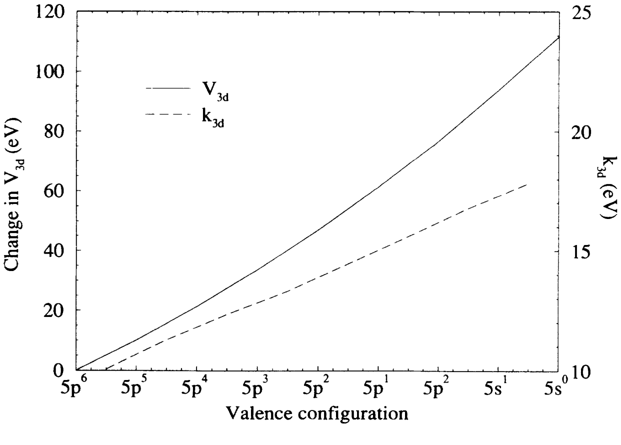

FIG. 2. Variation of the potential experienced by the Xe $3d$ electrons V_{3d}, given by the $3d$ eigenenergy, as a function of valence configuration. The right-hand axis is appropriate to k_{3d}, evaluated as the derivative of V_{3d} with respect to valence charge q, represented by the dashed line. k_{3d} is seen to be linear in q.

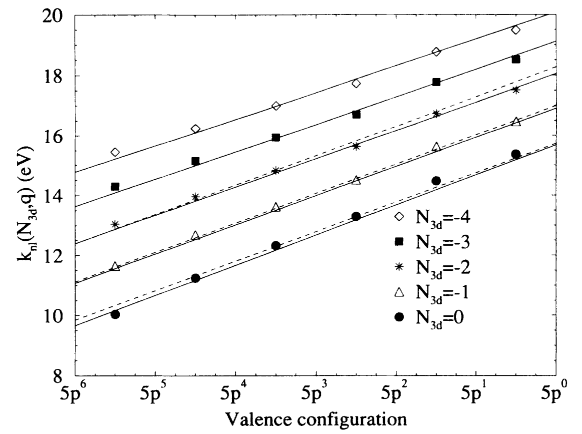

FIG. 3. Calculated values of $k_{3d}(N_{3d}, q)$ for Xe and numerical fits of the form $k(N, q) = a + bN + cN^2 + (d + eN)q$ (solid line) and $k(N, q) = a + bN + dq$ (dashed line). The abscissa is the valence configuration, and each line represents a separate core state. Species with 0, 1, 2, 3, and 4 holes in the 3d shell are represented.

These fits are shown by the solid and dashed lines in Fig. 3, respectively. By parametrizing V in this manner we can evaluate ξ as a reasonably short yet formally exact Taylor series. Neglecting terms with small coefficients c and e, we obtain from (3)

$$\Delta\xi = \Delta\left\{qb + \frac{dq}{dN}\left[a - 2b + d\left(q - \frac{dq}{dN}\right)\right] + \frac{dV^e}{dN}\right\}. \tag{13}$$

Since $k \sim \langle 1/r_v \rangle$, we note that b represents the contraction of the valence shell on core ionization, while the coefficient d corresponds to the expansion and/or contraction of the valence shell with gain and/or loss of valence charge. Examination of the nontransition elements from Na to Xe has shown that the inequality $b \gtrsim d$ observed for Xe is a general rule, and means that k for a core-ionized atom with a screening electron is slightly greater than k for the neutral atom. By the equivalent cores approximation this implies that k increases with Z across the Periodic Table:

$$\begin{aligned} k^Z(0, -Ze) &\leq k^Z(-1, -(Z+1)e) \\ &\approx k^{Z+1}(0, -(Z+1)e), \end{aligned} \tag{14}$$

corresponding to the gradual decrease in valence shell radius with Z. The comparison of $k(N_{3d})$ evaluated for $5s^2 5p^6$ to $5s^2 5p^5$ valence configurations for Xe[$N_{3d} = 0$], I[$N_{3d} = -1$], Te[$N_{3d} = -2$], and Sb[$N_{3d} = -3$] (see Table I) shows that the equivalent cores approximation works very well for k.

TABLE I. Comparison of $k(N_{3d})$ evaluated for $5s^2 5p^6$ to $5s^2 5p^5$ valence configurations for Xe[0], I[−1], Te[−2], and Sb[−3] illustrating the validity of the equivalent cores approximation for k.

Core	$k(N_{3d})$/eV
Xe[0]	10.05
I[−1]	9.98
Te[−2]	9.92
Sb[−3]	9.85

More generally, Eq. (13) should involve a summation over the different valence subshells with a separate k for s, p, and d states. In practice we find that it is not unreasonable to use a single k for s and p valence electrons, but not for d valence levels. Thomas and Weightman have pointed out[7] that the inequivalence of $k(q_{sp})$ and $k(q_d)$ means that analysis of measured Auger-parameter shifts can yield not only total charge transfer but also Δq_{sp} and Δq_d. In molecules or solids with unfilled d and sp bands in the ground state there is the possibility that a screening charge will fill the d band upon core ionization. In this event the derivatives of the potential suffer singularities at the point where a band fills and the expansions in Eq. (3) must be performed in two stages about points either side of the singularities.

V. DISCUSSION

Our study of atomic Xe shows that the core potential is surprisingly well represented by a low-order polynomial over a large range of q and N. The calculations suggest that the neglect of the q dependence of k is the origin of the failure of the Thomas-Weightman[7] expression to describe the metal-to-atom Auger-parameter shift for Mg. This is not surprising since atomic properties are perturbed by the chemical environment and in the case of metal-atom Auger-parameter shifts this means that the response of an atom to the availability of screening charge must be implicit in any theoretical model. Similar considerations will be important in understanding the Auger parameter and XPS shifts between materials of different charge state, such as comparison of atomic and strongly ionic systems.

Returning now to the Mg metal-atom Auger-parameter shift we see that the increase in $k(N,q)$ due to core ionization is offset by the presence of a screening charge, and Eq. (8) becomes

$$\xi_{\mathrm{metal}} - \xi_{\mathrm{atom}} = qb(\gamma - 1) + \gamma \left(\frac{dq}{dN}\right)_{\mathrm{metal}} \left[a - 2b + d\left\{q - \left(\frac{dq}{dN}\right)_{\mathrm{metal}}\right\}\right]. \tag{15}$$

Using Dirac-Fock calculations for Mg we have obtained

$$k^{\mathrm{Mg}}(N,q) = 12.0 - 2.4N - 0.1N^2 + (2.4 + 0.2N)q. \tag{16}$$

With these parameters, assuming $dq/dN = 1$ and imposing the constraint $\gamma > 1$ we calculate $\xi^{\mathrm{Mg}}_{\mathrm{metal}} - \xi^{\mathrm{Mg}}_{\mathrm{atom}} > 10.4$ eV consistent with the experimental value of 10.6 eV. Inserting the experimental Auger-parameter shift in (15) yields $\gamma^{\mathrm{Mg}} = 1.05$. Repeating this analysis for the group-IIB element Zn we find $\gamma^{\mathrm{Zn}} = 1.06$, while for the simple metal Na we obtain $\gamma^{\mathrm{Na}} = 1.10$. These results are shown in Table II along with the corresponding values of γ_{TW}. Although the empirically determined γ's satisfy the relation $1 < \gamma < \gamma_{\mathrm{TW}}$ they are little greater than 1, and hence atomic values of k are surprisingly good even for these metals. We note that perfect screening has been assumed for the metallic state. By the equivalent core approximation one expects that a core ionized site in Na metal, for example, will resemble a Mg impurity. On electronegativity grounds one would expect the core ionized site to have a net negative charge implying dq/dN may be slightly greater than 1 in metals. This would tend to reduce γ, and give k_{solid} even closer to the corresponding atomic value. The experimental error in measuring $\xi^{\mathrm{Mg}}_{\mathrm{metal}} - \xi^{\mathrm{Mg}}_{\mathrm{atom}}$ yields a corresponding ~ 4% error in γ, which is a significant improvement on the ~ 15% precision obtained with the truncation and renormalization algorithm. We conclude that empirically determined solid-state potential parameters will enable more reliable estimates of charge transfer to be deduced from Auger-parameter shifts.

TABLE II. Column 2 gives estimates of γ for Mg and Zn obtained by Thomas and Weightman (Ref. 7) (where the upper bound is γ_{TW}) using the renormalization and/or truncation algorithm. Empirical values for Na, Mg, and Zn determined from metal-free atom Auger-parameter shifts and having an uncertainty of ~5% are shown in column 3.

	Truncation and/or renomalization	$\gamma_{\mathrm{empirical}}$
Na		1.10
Mg	$1 < \gamma < 1.29$	1.05
Zn	$1 < \gamma < 1.30$	1.06

VI. CONCLUSIONS

A sound potential model is necessary if measurements of the changes in atomic-core potential are to be used to probe charge state. We have shown that the simple model in which the contribution to the core potential due to the valence charge density V^{valence} is assumed to be linearly proportional to the valence charge q does not describe the experimental metal-to-atom Auger-parameter shift of Na, Mg, and Zn. A study of atomic Xe shows that this constant of proportionality k is itself a function of valence state, implying that V^{valence} depends quadratically on q. The study of Xe suggests that the atomic-core potential is well described by $V^{\mathrm{valence}} = (a + bN)q + 0.5dq^2$, and the physical interpretation of these coefficients has been discussed. By evaluating a, b, and d from DF calculations for Na, Mg, and Zn atoms and taking experimental values of metal-atom Auger-parameter shifts we have shown that the solid-state renormalization constant γ, which relates the atomic value of $k(N,q)$ to its value in the solid, can be empirically determined. For these three elements γ is close to 1 meaning the k_{solid} are close to the atomic values.

The simple potential model discussed here describes atomic potentials very well. All the necessary model parameters can be determined from the results of first-principles atomic-structure calculations and their physical meaning is clear. The approach described provides a framework for straightforward yet reliable analysis of chemical shifts in terms of local charge state.

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