Received: 6 September 2019 | Revised: 8 February 2020 | Accepted: 24 February 2020

DOI: 10.1002/sia.6763

ECASIA SPECIAL ISSUE PAPER

Relationship between the Auger parameter and the ground state valence charge at the core-ionized site

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A simple semi-empirical model that correlates the Auger parameter to the ground state valence charge of the core-ionized atom with closed valence shell configuration, and which was previously applied to Cu(I) ($3d^{10}$) compounds, is extended to Ba (II) ($5d^{10}$), Pb (II) ($5d^{10}4s^2$), and Zn (II) ($3d^{10}$) compounds (halides and chalcogenides). Until now, the Auger parameter was employed to separate initial and final state effects that influence the core electron binding energy. In agreement with our model, a linear relationship is found between the Auger parameter shift and the ground state Bader valence charge obtained by density functional theory (DFT) calculations.

KEYWORDS

Auger parameter, *closed shell* configurations and *nonlocal* screening mechanism, core photoemissions and core-core′-core″ Auger transitions, XPS of Cu(I), Ba (II), Pb (II), and Zn (II) halides and chalcogenides

1 | INTRODUCTION

In a previous contribution, we reported a simple semi-empirical model that correlates the Auger parameter of a core-ionized atom with closed valence shell configuration to the ground state valence charge calculated by a Bader analysis of density functional theory (DFT) results, and we applied it to Cu(I) compounds.[1] Here, the model is also applied to Ba (II), Pb (II), and Zn (II) compounds (halides and chalcogenides), confirming its general use.

2 | INITIAL AND FINAL STATE CONTRIBUTIONS IN XPS AND THE AUGER PARAMETER

It is well-known that the binding energy of core electron depends on so-called initial and final state effects.[2]

As previously demonstrated, the general expression of the binding energy, referenced to the Fermi level, for the creation of a core hole in the orbital c_i of the atom in the solid under study, $E_b\ (c_i)^{FL}$ (atom/solid), may be written to a good approximation as[1,3]

$$E_b(c_i)^{FL}(\text{atom/solid}) = E_b(c_i)^{VL}(\text{free atom}) + k^0Q^0 - kQ + V_M - \Phi_{solid}\text{-}R(c_i), \quad (1)$$

where $E_b\ (c_i)^{VL}$ (free atom) is the binding energy of the free atom referenced to the vacuum level. The quantities Q^0 and Q represent the number of valence electrons of the free atom and of the atom in the solid under study, respectively; the two terms k^0Q^0 (free atom) and kQ (atom/solid) give the contribution to the core-ionization energy of the valence electrons with the factors k^0 and k that depend on the inverse of the valence shell radius of the free atom and the atom in the solid, respectively. V_M represents the Madelung site energy at the core-ionized ion and Φ_{solid} the work function of the solid, which is assumed to be in electrical equilibrium with the spectrometer. The local effective ground state valence charge at the core-ionized atom is $Q_{eff} = (Q^0 - Q)$. All these quantities are related to the initial state effects in X-ray photoelectron spectroscopy (XPS).[1-3]

The last term in Equation (1) represents the relaxation energy, ie, the energy taken up by the ejected core-electron (c_i) due to the internal reorganization of the valence electrons in the relaxation step that follows (or is concomitant to) the core-ionization step. ($R\ (c_i)$ is always >0, and therefore, $-R\ (c_i)$ decreases the electron binding energy.) This quantity represents the final state effects in XPS[1-3] and has two contributions:

$$R(c_i) = \left[R^a(Q) - R^a\left(Q^0\right)\right] + R^{ea}(\text{extra-atomic}). \qquad (2)$$

The first one represents the atomic relaxation energy, $[R^a(Q) - R^a(Q^0)]$, due to the difference in the valence electrons number between the atom under study and the free atom; the latter, R^{ea} (extra-atomic), represents the extra-atomic relaxation energy due to electrons from nearest-neighbour ligands moving to screen the core-ionized atom.

The atomic relaxation energy, $[R^a(Q) - R^a(Q^0)]$, is negative for a positive ion, $Q_{eff} = (Q^0 - Q) > 0$, and positive for a negative ion, $Q_{eff} = (Q^0 - Q) < 0$, ie, the ground state electron charge is reduced or increased with respect to the free atom. The extra-atomic relaxation energy, R^{ea} (extra-atomic), is instead always a positive quantity.

The Madelung site energy, V_M, which depends on Q_{eff}, is negative for a positive ion and positive for a negative ion (for a positive ion, the Madelung site energy decreases the electron binding energy).

The Auger parameter, α', was defined by Wagner[1-3] by the general equation

$$\alpha' = E_b^{FL}(c_1) + E_k^{FL}(c_1 c_2 c_3). \qquad (3)$$

The kinetic energy of the Auger ($c_1c_2c_3$) electron and the binding energy of a core (c_1) electron, from the atom under study, recorded in the same spectrum, are added together to obtain a quantity that does not depend on the reference level (the vacuum or the Fermi level) and, in the case of insulating or semiconductor-type solids, does not depend on any charging phenomena either. In the Auger process, the initial core hole, c_1, is filled by the c_2 electron while the c_3 electron escapes from the solid surface leaving the atom with two core-holes.

The kinetic energy of the Auger transition may be written as[1-3]

$$E_k^{FL}(c_1 c_2 c_3) = E_b^{FL}(c_1) - E_b^{FL}(c_2) - E_b^{FL}(c_3) - U(c_2 c_3), \qquad (4)$$

where $U(c_2c_3)$ represents the effective repulsion energy between the c_2 and c_3 holes in the final state of the Auger process.

It is possible to demonstrate that the Auger parameters shifts for the atom in the solid under study, with respect to the free atom, can be written as[1,3]

$$\alpha'(\text{atom/solid}) - \alpha'(\text{free atom}) = 2R(c_1) = 2\left[R^a(Q) - R^a\left(Q^0\right)\right] + 2R^{ea}(\text{extra-atomic}). \qquad (5)$$

Equation (5) shows that the relaxation (polarization) energy, which is a valuable piece of chemical information, can be obtained experimentally by using the Auger parameter shift between the two chemical states.

Note that to derive Equation (5), it is assumed that $[E_b^{FL}(c_1) - E_b^{FL}(c_2)] \approx$ constant, that is, the binding energy shift for different core levels is about the same and independent from the chemical state. When this condition cannot be applied, as in case of P and S containing compounds—where the 2p core levels of S and P are spatially modified by alteration of the atomic environment and can only be considered *core-like* and not true core-type as the 1s electrons—a different approach is necessary to link the Auger parameter shift with the relaxation energy, as discussed in Moretti and Beck[1] and Moretti[3] and by Hohlneicher et al.[4]

Before discussing the model that relates $\Delta\alpha'$ to the ground state valence charge at the core-ionized site, Q_{eff}, it is helpful to recall that, according to Veal and Paulikas,[5] two main channels are open for the final state relaxation mechanism: the *nonlocal* and the *local* screening.

The *nonlocal* screening mechanism occurs when the core-ionized atom has a closed valence shell configuration. In this case, the relaxation energy depends essentially on the electronic polarizability of the nearest-neighbour ligands: On increasing the ligand polarizability, the final state relaxation energy increases. The polarization of the ligands may be seen as an electron transfer from the nearest-neighbours ligands towards the *spatially extended sp valence orbitals* of the core-ionized atom. The Auger parameter is expected to be very sensitive to the chemical nature of the nearest-neighbour ligands of the core-ionized atom. On the contrary, when the core-ionized atom has an open valence shell configuration, as in the case of Cu(II) ($3d^9$) compounds, the screening mechanism is *local*: An electron transfer occurs from the nearest-neighbour ligands into the *localized d atomic orbital* of the core-ionized d transition metal ions with an Auger parameter shift practically independent on the chemical state and similar to that measured for the metallic state (see, for details, Moretti and Beck[1]).

The Auger parameter data for Cu(I), Ba (II), Pb (II), and Zn (II) halides and chalcogenides are taken from the National Institute of Standards and Technology (NIST) database[6] (for Cu(I) compounds, see also caption to Figure 1). The Auger parameter for the free atoms, M(g) (M = Cu, Ba, Pb, and Zn), used to calculate the Auger parameter shifts and to draw the $\Delta\alpha'$ vs Q_{eff} plots is reported in Figures 1–4, taken from references reported in the captions to these figures. The ground state Bader valence charge, Q_{eff}, was obtained by DFT calculations as described in the next chapter.

3 | GROUND STATE VALENCE CHARGE AND FINAL STATE EFFECTS

The ground state valence charges at the cationic Cu(I), Ba (II), Pb (II), and Zn (II) sites, in the halides and chalcogenides compounds, were calculated by analysing DFT results according to the Bader definition.[9] All calculations within the DFT formalism were performed using the VASP 5.2 package[10,11] together with the projector-augmented-wave (PAW) method of Blöchl[12] and the GW potentials as proposed by Perdew et al.[13]

An important merit of the Bader analysis is that the electron density does not depend on the computational scheme chosen, once the level of theory is adequate; ie, the basis set encompasses both polarization and diffuse functions.

To develop our model that links the Auger parameter shift, $\Delta\alpha'$, to the ground state valence charge at the core-ionized site, Q_{eff}, we need to know the *atomic relaxation energy per valence electron*, R_1^a.

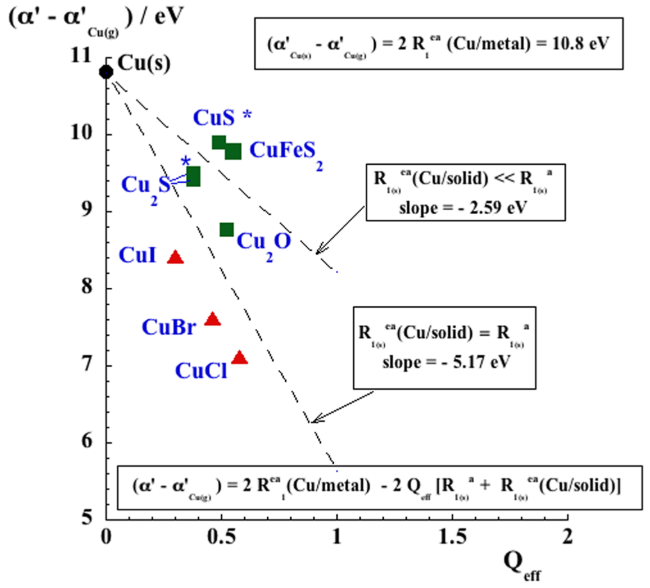

FIGURE 1 Auger parameter shift for copper in Cu(I) compounds with respect to the Cu-free atom vs the ground state Bader valence charge. The data for Cu(g)—$E_b^{VL}(2p_{3/2})$ = 939.70 eV, $E_k^{VL}(L_3M_{45}M_{45},{}^1G)$ = 900.70 eV, and α′ = 1840.40 eV—are from Aksela S, Sivonen J. Phys Rev A 1982; 25; 1243–1246, and Aksela H, Aksela S, Patana H. Phys Rev A 1984; 30; 858–864. XPS data are from Biesinger,[7] apart the data for CuS (covellite) and Cu_2S (chalcocite), indicated with the symbol (*), that are from Perry DL, Taylor JA. X-ray photoelectron and Auger studies of Cu2S and CuS. J Mat Sci Letters 1986; 5; 384-386. The experimental results for CuS and $CuFeS_2$ (with copper in nominal Cu(II) oxidation state but absence of the $2p_{3/2}$ satellite peak) are in better agreement with Equation (19)

This quantity may be estimated from numerical Hartree-Fock calculations of core electron binding energies for free atoms and ions reported by Broughton and Bagus.[14] The unrelaxed Eigenvalue (Koopmans' theorem) and the relaxed (ΔSCF) core-ionization energies are calculated by self-consistent Hartree-Fock programs, which do not include relativistic corrections, and hence the energies are only for the Russell-Saunders $^{(2S+1)}L$ multiplets. These multiplets correspond to the weighted average of the observed spin-orbit states. The difference between the Eigenvalue and the ΔSCF value represents the atomic relaxation energy:

$$\Delta SCF = \text{Eigenvalue} - R^a. \tag{6}$$

Equation (1) applied to a free ion gives[1]

$$\Delta\Delta SCF = E_b(c_i)^{VL}(\text{free ion}) - E_b(c_i)^{VL}(\text{free atom}) = \Delta\text{Eigenvalue} - \Delta R^a, \tag{7}$$

$$\Delta\text{Eigenvalue} = k^0Q^0 - kQ \quad , \tag{8}$$

$$\Delta R^a = \left[R^a(Q)\text{-}R^a\left(Q^0\right)\right]. \tag{9}$$

The atomic relaxation shift for a cationic species, ΔR^a, may be approximated by the equation

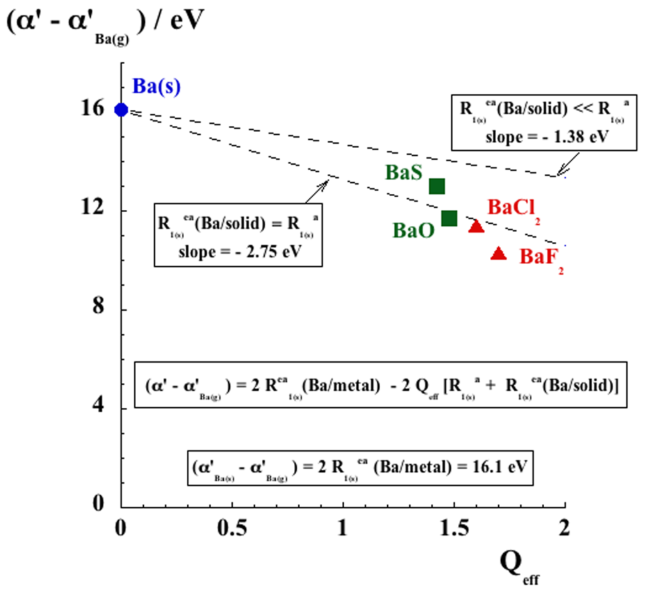

FIGURE 2 Auger parameter shift for barium in Ba (II) compounds with respect to the Ba-free atom vs the ground state Bader valence charge. The data for Ba(g)—$E_b^{VL}(3d_{5/2})$ = 988.7 eV, $E_k^{VL}(M_4N_{45}N_{45})$ = 576.8 eV, and α′ = 1365.5 eV—are from Kellokumpu M, Aksela H. Phys Rev 1985; 31; 777–782, and Aksela H, Aksela S, Tulkki J. Phys Rev A 1993; 47; 4865–4873. X-ray photoelectron spectroscopy (XPS) data are from the National Institute of Standards and Technology (NIST) database[6] (see Beck and Moretti[8] for details)

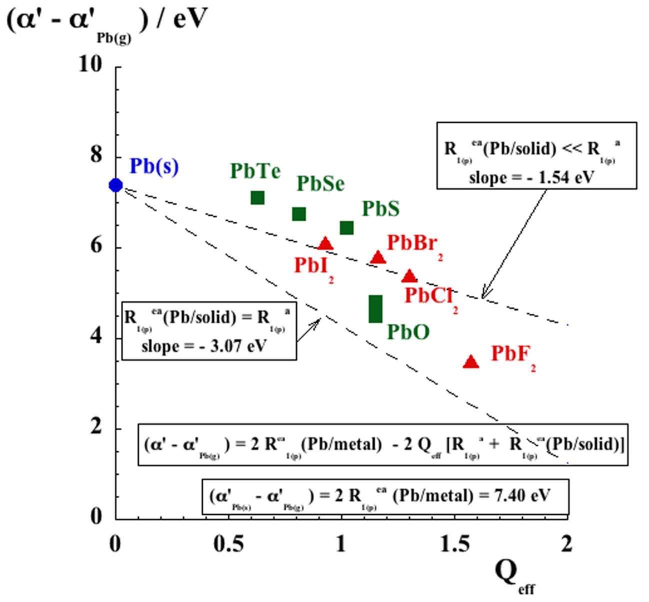

FIGURE 3 Auger parameter shift for lead in Pb (II) compounds with respect to the Pb-free atom vs the ground state Bader valence charge. The data for Pb(g)—$E_b^{VL}(4f_{7/2})$ = 144.30 eV, $E_k^{VL}(N_6O_{45}O_{45})$ = 81.3 eV, and α′ = 225.6 eV—are from Patanen M, Urpelainen S, Kantia T, Heinasmaki S, Aksela S, Aksela H. Phys Rev A 2011; 83; 053408–1-5. X-ray photoelectron spectroscopy (XPS) data are from the National Institute of Standards and Technology (NIST) database[6] (see Beck and Moretti[8] for details). The experimental results, apart from PbO and PbF_2, are in better agreement with Equation (19)

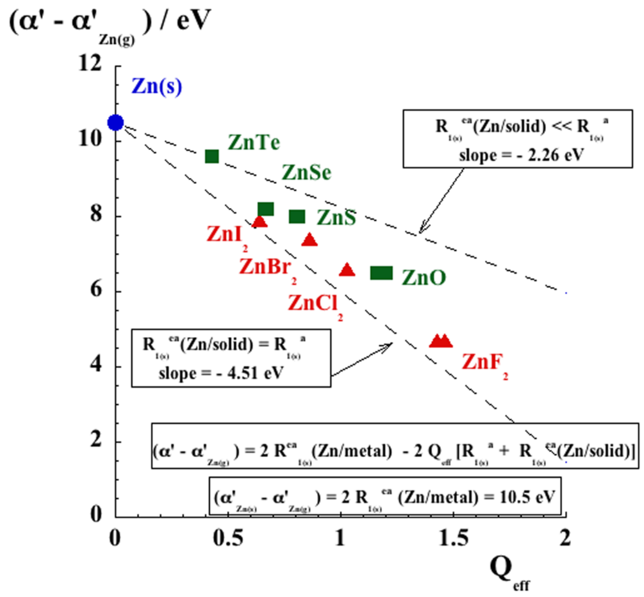

FIGURE 4 Auger parameter shift for zinc in Zn (II) compounds with respect to the Zn-free atom vs the ground state Bader valence charge. The data for Zn(g)—$E_b^{VL}(2p_{3/2})$ = 1028.9 eV, $E_k^{VL}(L_3M_{45}M_{45},{}^1G)$ = 974.4 eV, and α′ = 2003.3 eV—are from Aksela H, Aksela S, Patana H. Phys rev a 1984; 30; 858–864. X-ray photoelectron spectroscopy (XPS) data are from the National Institute of Standards and Technology (NIST) database[6] (see Beck and Moretti[8] for details). The experimental results for ZnTe are in better agreement with Equation (19)

$$\left[R^a(Q) - R^a\left(Q^0\right)\right] \approx -Q_{eff}R_1^{\,a}, \tag{10}$$

where $R_1^{\,a}$ represents *the atomic relaxation energy per valence electron.*

Therefore,

$$\Delta\Delta SCF = k^0Q^0 - kQ + Q_{eff}R_1^{\,a}. \tag{11}$$

Details on the calculation of $R_1^{\,a}$ values based on the Broughton and Bagus data[14] and Equation (11) are reported in Moretti and Beck[1] (Cu) and Beck and Moretti[8] (Ba, Pb, and Zn). The $R_1^{\,a}$ values for the free atoms are as follows: Cu (2p core hole, 4s electron): $R_{1(s)}^{\,a}$ = 1.29 eV; Ba (3d core hole, 6s electron): $R_{1(s)}^{\,a}$ = 0.688 eV; Pb (4f core hole, 6p electron): $R_{1(p)}^{\,a}$ = 0.768 eV; Zn (2p core hole, 4s electron): $R_{1(s)}^{\,a}$ = 1.13 eV.

4 | AUGER PARAMETER SHIFT AND GROUND STATE VALENCE CHARGE FOR Cu(I), Ba (II), Pb (II), AND Zn (II) COMPOUNDS

According to Equation (10), the lost atomic relaxation energy can be written as

$$R^a(M/solid) \approx -Q_{eff}R_1^{\,a}, \tag{12}$$

where M/solid represents the cationic species Cu(I), Ba (II), Pb (II), or Zn (II) in the solid compounds under study, with the respective values of Q_{eff} and $R_{1(s)}^{\,a}$ or $R_{1(p)}^{\,a}$, calculated as reported in the previous section.

It is generally assumed that in the metallic state, there is a complete screening of the core hole, ie, *one electron* moves towards the core-ionized atom in the final state. The relaxation energy $R_1^{\,ea}$(M/metal) is related to the Auger parameter shifts according to Equation (5):

$$[\alpha'(M/metal) - \alpha'(M(g))] = 2\,R_1^{\,ea}(M/metal). \tag{13}$$

For Cu(I), Ba (II), Pb (II), and Zn (II) compounds, the *nonlocal* screening mechanism involves an electron transfer from the nearest-neighbour ligands towards the spatially extended 4s, 6s, 6p, or 4s valence orbitals, respectively.

The relaxation energy due to the *hypothetical* charge transfer of Q_{eff} electrons from the ligands to the spatially extended sp orbital of the cation (M/solid), equal to $Q_{eff}\,R_1^{\,ea}$, and the charge transfer of one more electron, $R_1^{\,ea}$, would lead to a core-ionized cation (M/solid), with the same number of electrons in the sp orbitals as for a relaxed core-ionized atom in the metal (M/metal).

According to this hypothesis, we can write the *full screening equation for the cation in the M/solid compounds*:

$$R_1^{\,ea}(M/metal) \approx Q_{eff}R_1^{\,ea}(M/solid) + R_1^{\,ea}(M/solid); \tag{14}$$

therefore

$$R_1^{\,ea}(M/solid) \approx R_1^{\,ea}(M/metal) - Q_{eff}R_1^{\,ea}(M/solid). \tag{15}$$

The Auger parameter shift becomes

$$\begin{aligned}[\alpha'(M/solid) - \alpha'(M(g))] &= 2\,R^a(M/solid) + 2\,R^{ea}(M/solid)\\ &= -2\,(Q_{eff})\,R_1^{\,a} + 2\,[R_1^{\,ea}(M/metal) - (Q_{eff})\,R_1^{\,ea}(M/solid)]\\ &= 2\,R_1^{\,ea}(M/metal) - 2\,Q_{eff}[R_1^{\,a} + R_1^{\,ea}(M/solid)],\end{aligned} \tag{16}$$

and considering Equation (13),

$$[\alpha'(M/solid) - \alpha'(M(g))] = [\alpha'(M/metal) - \alpha'(M(g))] - 2\,Q_{eff}[R_1^{\,a} + R_1^{\,ea}(M/solid)]. \tag{17}$$

To check the validity of Equation (17), the following two limiting cases are considered:

1. $R_1^{\,a} \approx R_1^{\,ea}$ (M/solid)
2. $R_1^{\,a} > > R_1^{\,ea}$ (M/solid)

Case 1 leads to a linear relationship Δα′ vs Q_{eff} with the larger negative slope of $-4R_1^{\,a}$ and intercept [α′(M/metal) − α′(M(g))]:

$$[\alpha'(M/solid) - \alpha'(M(g))] = [\alpha'(M/metal) - \alpha'(M(g))] - 4Q_{eff}R_1^{\,a}. \tag{18}$$

Case 2 leads to a linear relationship $\Delta\alpha'$ vs Q_{eff} with the smaller negative slope of $-2R_1{}^a$ and intercept $[\alpha'(M/metal) - \alpha'(M(g))]$:

$$[\alpha'(M/solid) - \alpha'(M(g))] = [\alpha'(M/metal) - \alpha'(M(g))] - 2Q_{eff}R_1{}^a. \quad (19)$$

Considering the simplicity of our semi-empirical model, the results shown in Figures 1–4 are encouraging: The relationship between the Auger parameter and the ground state valence charge for Cu(I), Ba (II), Pb (II), and Zn (II) compounds is confirmed to a good approximation (for details about the crystal structure of the compounds and the relative valence charges, see Moretti and Beck[1] and Beck and Moretti.[8] This $\Delta\alpha'$ vs Q_{eff} relationship could represent a convenient way to obtain the ground state valence charge. In fact, the use of Equation (1) is more demanding because we have to know the atomic factors k^0 and k and the quantities V_M and Φ_{solid}, which depend on the crystal structure and on Q_{eff}. In a following paper, we will report in detail the application of Equation (1) to obtain Q_{eff} considering both the difficulties in its use, especially due to the unknown quantity Φ_{solid}, and the way to cope with them.[8]

5 | CONCLUSIONS

The core electron binding energy is affected by the so-called initial and the final states effects, while the Auger parameter depends, to a good approximation, only on the final state effects. We have developed a simple semi-empirical model that correlates the Auger parameter shifts to the ground state valence charge of the core-ionized atom with closed valence shell configuration. In agreement with our model, a linear relationship is found between the Auger parameter shift and the ground state Bader valence charge for Cu(I), Ba (II), Pb (II), and Zn (II) halides and chalcogenides obtained by DFT calculations. The relaxation process in these compounds is *nonlocal*, because of an electron transfer from the nearest-neighbour ligands towards the spatially extended sp valence orbitals of the core-ionized ion. The relationships shown in Figures 1–4 could also be reported as $\alpha'(M/solid) = \alpha'(M/metal) - 2Q_{eff}R_1{}^a$ and $\alpha'(M/solid) = \alpha'(M/metal) - 4Q_{eff}R_1{}^a$, without taking into account the Auger parameter shifts with respect to the metal free atom. This is generally very useful because the Auger parameter of free atoms is available only for a few elements.

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How to cite this article: Moretti G, Beck HP. Relationship between the Auger parameter and the ground state valence charge at the core-ionized site. *Surf Interface Anal*. 2020;1–5. https://doi.org/10.1002/sia.6763