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Initial and final state contributions to binding-energy shifts due to lattice strain: Validation of Auger parameter analyses

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Abstract

The validity of Auger parameter analyses to separate initial and final state contributions to core-level binding energy shifts in the growth of nanoparticles is tested; the specific concern is shifts due to lattice strain. Theoretical energies for the hole-states involved are used to avoid the approximations and assumptions normally required to justify the analyses. When the Auger transitions involve states with high lying d-holes, the Auger parameter analysis of the origin of the shifts is incorrect. When only core–hole Auger states are used, a suitable formulation will accurately reproduce the initial state origin of shifts due to lattice strain.

The separation of core-level binding energy, BE, shifts into contributions from initial and final state effects is quite important. Initial state effects reflect ground state chemistry and, hence, the information that they provide may be relevant for understanding other chemical processes and reactions. On the other hand, final state effects arise from the properties of short lived, highly-excited core–hole states and are less relevant for most chemical processes [1,2]. It is possible to separate initial from final state effects using ab initio wavefunctions, WFs [2–4]. Initial state BEs, BE(Initial), and BE shifts, ΔBE(Initial), are obtained by forming an initial state WF for the core-level ion using Hartree–Fock, HF, optimized orbitals for the initial state where relaxation and screening effects are not taken into account [2]. These ionic WFs are properly characterized as frozen orbital, FO, WFs. When screening and relaxation are taken into account by using a WF and orbitals self-consistent field, SCF, optimized for the core–hole state, one obtains BE(ΔSCF) and ΔBE(ΔSCF) that represent both initial and final state effects. Finally, the relaxation energy, $E_R = \mathrm{BE(Initial)} - \mathrm{BE}(\Delta\mathrm{SCF})$, and its shift, ΔE_R, represent the pure final state contribution.

There are also approaches based on the work of Wagner [5] that combine measured Auger electron kinetic energies, E_{kin}, with X-ray photoemission spectroscopy, XPS, measurements of the BEs to separate the ΔBE(Initial) and ΔE_R contributions to BE shifts. The Wagner Auger parameter for the ith core-level, $\alpha(i)$, and its shifts, $\Delta\alpha(i)$, are:

$$\alpha(i) = \mathrm{BE}(i) + E_{kin}(klm) \quad \text{and}$$
$$\Delta\alpha(i) = \Delta\mathrm{BE}(i) + \Delta E_{kin}(klm), \tag{1}$$

where i, k, l, and m are core levels. With several approximations, the $\Delta\alpha(i)$ can be related to $\Delta\mathrm{BE}(i,\mathrm{Initial})$ and $\Delta E_R(i)$ by

$$\Delta E_R(i) = \Delta\alpha(i)/2 \quad \text{and}$$
$$\Delta\mathrm{BE}(i,\mathrm{Initial}) = \Delta\mathrm{BE}(i) + \Delta\alpha(i)/2. \tag{2}$$

The validity of the approximations used to derive these relations has been discussed extensively [1,5–10]. In particular, Hohlneicher et al. [10] extended the work of Wagner to reduce the approximations and developed a modified Auger parameter, $\beta(i)$, with

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$$\beta(i) = E_{\mathrm{kin}}(kii) + 2\mathrm{BE}(i) - \mathrm{BE}(k) \quad \text{and}$$
$$\Delta\beta(i) = \Delta E_{\mathrm{kin}}(kii) + 2\Delta\mathrm{BE}(i) - \Delta\mathrm{BE}(k) \tag{3}$$

where i and k are core levels. They derived relationships similar to those for $\Delta\alpha$:

$$\Delta E_{\mathrm{R}}(i) = \Delta\beta(i)/2 \quad \text{and}$$
$$\Delta\mathrm{BE}(i, \mathrm{Initial}) = \Delta\mathrm{BE}(i) + \Delta\beta(i)/2. \tag{4}$$

In the $\Delta\beta$ analysis, it is not necessary to assume that the BE's of all core levels have equal shifts. This is especially important and relevant when we consider the high precision required for the decomposition of total shifts when ΔBE is $\sim$1 eV as found for supported metal clusters [11,12]. Previous work with Auger parameter analyses has depended on assumptions and approximations that are not fully tested and there are conflicting claims about the validity of the Wagner formalism [1,6–8,10]. In this Letter, we make definitive tests of the validity of the $\Delta\alpha$ and $\Delta\beta$ Auger parameter formalisms by using ab initio energies for the electronic states required to calculate α and β.

The particular example that we consider relates to the ΔBE of particles supported on inert, oxide surfaces where there are typically shifts of the BEs of small particles to the bulk BE of $\sim$1.0 eV to smaller BE for the bulk [1,4,9,11,12]. There is substantial controversy over the initial or final state origin of these shifts. For Cu particles supported on Al_2O_3, Wu et al. [11] reported that, for very small particles, the initial state contributions for the $2p_{3/2}$ BE were to smaller BE, ΔBE(Initial) ≈ -0.8 eV, which was counter balanced by a large $\Delta E_{\mathrm{R}} \approx -1.8$ eV to give ΔBE = ΔBE(Initial) $- \Delta E_{\mathrm{R}} \approx +1.0$ eV. In contrast, Luo et al. [12] report that the ΔBE(initial) for the $3d_{5/2}$ XPS of Ag particles on Al_2O_3 is small and negative at 0.04 monolayer coverage, with ΔBE(Initial) $= -0.06$ eV. The ΔBE(Initial) becomes positive at slightly higher Ag coverage and reaches a maximum of ΔBE(Initial) $= +0.1$ eV. Both Wu et al. [11] and Luo et al. [12] used the Wagner $\Delta\alpha$ formulation and used Auger transitions from the highest d levels, 3d for Cu and 4d for Ag, to fill the core–hole, denoted C. Since the d electrons participate in the bonding of these noble metals and can be considered as part of the metal valence, V, levels, these Auger transitions may be described as CVV. With the $\Delta\beta$ Auger parameter [10] and using an Auger transition involving only core levels, Richter et al. [4] found, for Co particles on Al_2O_3, that the initial state contribution to the particle size shift of the 3p BE was +0.3 eV or $\sim$30% of ΔBE(3p) = +0.98 eV. This result is in contradiction to the results for Cu and Ag [11,12] obtained with the Wagner $\Delta\alpha$ and using CVV Auger transitions. The Auger parameter analysis of Richter et al. [4] was supported by the ΔBE calculated from ab initio WFs for isolated Cu clusters where the lattice strain due to a contraction of $\sim$5% in small clusters was shown to contribute a +0.5 eV increase in the ΔBE(Initial), $\sim$50% of the total ΔBE.

Furthermore, it was shown [4] that this ΔBE(Initial) arose from the increased d involvement in the bonding and materials chemistry of the Cu particle when the lattice was contracted. Thus, our particular concern is to identify how well the $\Delta\alpha$ and $\Delta\beta$ Auger parameters can provide reliable decompositions into initial and final state contributions to the ΔBE due to lattice strain. This will be done with a small cluster model of Ag where we have determined WFs for all the electronic states involved in the ionization and Auger processes. The values of $\Delta\alpha$ and $\Delta\beta$ obtained with these WFs will be compared to the ΔE_{R} and ΔBE(Initial) obtained with FO and ΔSCF WFs. The cluster model and HF WFs that we use here have been shown to accurately describe the final state core–hole screening as a function of particle size [4] as well as the closely related screening of a point charge above a metal surface [13]. Thus, our model will provide definitive tests of the approximations used in Auger parameter analyses.

The cluster model of Ag_{13}, see Fig. 1, has the geometry of bulk fcc Ag and contains a central Ag atom with the full, 12-fold, coordination of a bulk atom; it is this atom that is core ionized. The starting Ag–Ag nearest neighbor, NN, distance, $r(\mathrm{NN}) = 5.46$ bohr $= 2.9$ Å, is taken from the bulk lattice constant; lattice strain is modeled by varying r(NN) in steps of 0.1 bohr keeping the fcc geometry. In all cases, shifts are taken with respect to the value at the bulk r(NN). All the electrons of the central atom are included in the WF while an effective core potential, ECP, is used to treat the Ar + 3d cores of the 12 edge atoms [14]. Since the Ag 4d electrons are included, their contribution to the bonding is taken fully into account. The central atom was treated non-relativistically while the ECP for the edge atoms included scalar relativistic effects. The non-relativistic treatment of the central atom will have a substantial effect on the magnitudes of the calculated BEs; however, this error is expected to be essentially constant for the various lattice strains and it will not affect the BE shifts. The basis set for the all electron Ag atom is taken from the tabulation provided by Ahrlichs

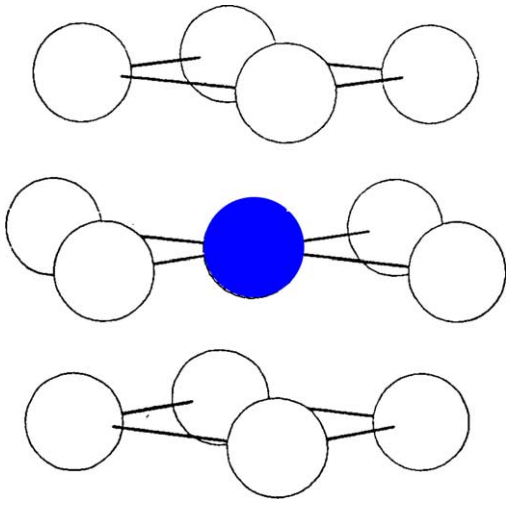

Fig. 1. The 13 atom model used to study lattice strain for Ag particles. The central atom, shown as shaded, is the atom that is core ionized.

and May [15] and the ECP basis set from Hay and Wadt [14]. In both cases, the tabulated basis sets were enhanced to insure full participation of the Ag 5p in the cluster conduction band. Ab initio HF Cluster WFs are computed for the unionized and core-level ionized states of Ag_{13} and Ag_{13}^{+}. Since there is an odd number of electrons in Ag_{13}, the initial and final, ionic states as well as the Auger double-hole states are multiplet split [16]. These multiplet splittings are artifacts of the small cluster size and we consider the configuration average for all states [16,17].

For 3d, or $M_{4,5}$, ionization, ΔBE(Initial) and ΔBE(ΔSCF) are reported in Table 1; however, values of the ΔBE for other L and M shell core-levels are very similar. Although $d_{3/2}$ and $d_{5/2}$ spin–orbit splitting is not included in our WFs, the octahedral environment of the central Ag atom leads to a small, ~0.01 eV, splitting of the 3d BEs of t_{2g} and e_g symmetry; average values of the BEs and the Auger parameters over t_{2g} and e_g are given. HF WFs and energies are also determined for several different final, two hole, ionic states and used to obtain the Auger E_{kin} to these states; the $\Delta\alpha$ and $\Delta\beta$ Auger parameter shifts obtained with these theoretical E_{kin} and related theoretical BEs, see Eqs. (1)–(4), are given in Table 2.

A double ion that can represent a case where localized d-electrons are removed to form the Auger final state is one where two electrons are removed from an orbital that has e_g symmetry. Since the d orbitals of the central atom belong to e_g and t_{2g} point group representations of O_h, an e_g orbital can be fully localized on the central atom, fully delocalized over all atoms, or have some intermediate degree of localization. We ionized the lowest lying e_g orbital in the cluster d-band in the belief that an orbital with a deeper orbital energy is more likely to be localized than an orbital with a higher, less negative, orbital energy that may prefer to become involved in covalent bonds. This lowest lying e_g orbital has an orbital energy within 0.2 eV of the bottom of the d-band of the Ag_{13} particle. A large degree of localization of the holes in the Auger final double-hole state is believed to be required in order for the Auger transition to be suitable for use in a Wagner Auger parameter analysis [5–9]. Furthermore, it has been assumed that the Ag 4d orbitals are suitable for an Auger transition that will give a meaningful Auger parameter decomposition [6,11,12]. By contrast, in our approach the degree of localization is found by solving variational equations for the WF; it is not necessary to make any assumptions about this localization as is the case with conventional approaches [5–9,12]. We denote this final double hole state as dd_{loc}, to indicate that localization is possible; the associated Auger transition to fill the $M_{4,5}$ core–hole is denoted $M_{4,5}dd_{loc}$. For the dd_{loc} state, we take the coupling of the e_g^2 open shell to be $^3A_{2g}$; we make this exception to our rule of using configuration averages to have the greatest possibility that the d-shell hole will be localized [16]. In addition to the dd_{loc} state, we consider a double hole in a d-level of a_{1u} symmetry where, because of the symmetry, the hole cannot localize on the central Ag atom but must be delocalized; the results for this state are denoted dd_{deloc}.

We also consider a fully core Auger transition ($M_{4,5}N_1N_1$) where the double hole state leaves the 4s orbital on the central Ag atom empty. For these three Auger transitions, we use the Auger E_{kin} and BE(ΔSCF) obtained with our ab initio HF WFs to determine $\Delta\alpha$. For ($M_{4,5}N_1N_1$), we also determine $\Delta\beta$ [10] since this purely core–hole Auger transition meets the more stringent criteria for $\Delta\beta$.

The directly computed Ag(3d) BE shifts, ΔBE(ΔSCF), ΔE_R, and ΔBE(Initial), are given in Table 1 for r(NN) between 5.16 bohrs, which is a ~5% lattice contraction of the bulk r(NN) = 5.46 and 5.56 bohrs, which is a ~2% lattice expansion. A theoretical method that constrains the SCF variations [2,18] is used to separate the contributions to ΔBE(Initial) that arise from the 5sp conduction band electrons and from the 4d electrons. In Table 1, the former contributions are denoted 5sp Only while the latter are denoted 4d Added. The shifts in E_R, ΔE_R, with variation of the lattice constant are very small; see Table 1. Thus,

Table 1
The decomposition of BE shifts for the 3d BE of an Ag_{13} cluster into initial and final state effects

r(NN) bohr	5.16	5.26	5.36	5.46 (bulk)	5.56
ΔBE(ΔSCF)	+0.48	+0.29	+0.13	0	−0.11
ΔE_R	+0.03	+0.03	+0.01	0	−0.02
ΔBE(Initial)	+0.51	+0.32	+0.15	0	−0.13
5sp Only	−0.34	−0.23	−0.13	0	+0.12
4d Added	+0.83	+0.54	+0.27	0	−0.24

The shifts are for changes in the cluster lattice constant from the bulk nearest-neighbor distance, r(NN) = 5.46 bohr. The ΔBE as given by direct calculations of the initial and final state cluster wavefunctions are ΔBE(ΔSCF), ΔBE(Initial), and ΔE_R; For the ΔBE(Initial), the individual contributions from the conduction band 5sp electrons, labeled 5sp Only, and from the 4d electrons, labeled 4d Added, as obtained from constrained variations are also given. All energies are in eV.

Table 2
Auger parameter decompositions, $\Delta\alpha$ and $\Delta\beta$, into initial state, ΔBE(Initial), and final state, ΔE_R, for the Ag 3d BE shifts due to lattice strain in the Ag_{13} cluster are compared to the results obtained with the FO and ΔSCF WFs, denoted Exact (WF), and without using Auger energies

r(NN) bohr	5.16	5.26	5.36	5.46 (bulk)	5.56
Relaxation shifts – ΔE_R					
Exact (WF)	+0.03	+0.03	+0.01	0	−0.02
$M_{4,5}dd_{loc} - \Delta\alpha$	+0.30	+0.17	+0.07	0	−0.06
$M_{4,5}dd_{deloc} - \Delta\alpha$	+0.69	+0.44	+0.21	0	−0.18
$M_{4,5}N_1N_1 - \Delta\alpha$	−0.12	−0.07	−0.03	0	+0.05
$M_{4,5}N_1N_1 - \Delta\beta$	−0.01	0.00	0.00	0	+0.01
Initial state shifts – ΔBE(Initial)					
Exact (WF)	+0.51	+0.32	+0.15	0	−0.13
$M_{4,5}dd_{loc} - \Delta\alpha$	+0.78	+0.46	+0.21	0	−0.16
$M_{4,5}dd_{deloc} - \Delta\alpha$	+1.17	+0.73	+0.34	0	−0.29
$M_{4,5}N_1N_1 - \Delta\alpha$	+0.36	+0.22	+0.10	0	−0.06
$M_{4,5}N_1N_1 - \Delta\beta$	+0.48	+0.29	+0.13	0	−0.10

The Auger transitions for the Auger parameter analyses are identified. The lattice strain is modeled by varying the nearest-neighbor distance, r(NN). All energies are in eV.

it is meaningful to decompose the sp and 4d contributions to ΔBE(Initial) in order to establish how the chemistry related to lattice strain affects the BE shifts. The total ΔBE(Initial) is 0.5 eV for a lattice contraction of 5%, see Table 1, and this is about half of the total BE shift observed from small to large Ag particles [12]. With the decomposition of ΔBE into 5sp and 4d contributions, it is possible to identify the chemical origins of the BE shift.

The BE shift arises from the cancellation of a shift to lower binding energy from the 5sp conduction band and of a shift to higher binding energy from the participation of the Ag 4d electrons in the chemical bonding within the particle. The directions of the individual contributions are exactly as expected [2,4]. Lattice contraction increases the density of conduction band electrons around the core ionized Ag atom and this increased electron density leads to an electrostatic potential that lowers the core-level BEs [2]. The d participation in the chemical bonding within the particle can be viewed as a d hybridization; when electrons are promoted out of the compact d band, the resulting change in the electrostatic potential raises the core-level BEs [2,4]. These electrostatic effects of lattice contraction will be discussed, in more detail, elsewhere [19]. Here, our concern is to determine how well the $\Delta\alpha$ and $\Delta\beta$ Auger parameter analyses are able to correctly identify the initial state effect of lattice contraction.

In Table 2, we compare the relaxation shifts, ΔE_R, and the initial state shifts, ΔBE(Initial), obtained from our analysis of the hole state WFs with the Auger parameter decompositions, $\Delta\alpha$ and $\Delta\beta$. The data from the hole state WFs, in rows labeled Exact (WF), are taken from Table 1. The Auger parameter results, using calculated energies for the relations of Eqs. (1)–(4), are in rows labeled with an Auger transition. If the assumptions made in deriving the relationships between the shifts of the Auger parameter, $\Delta\alpha$ and $\Delta\beta$, and the ΔE_R and ΔBE(Initial) are correct, these values should be very similar to those for the Exact WF theory.

When the Auger transitions involve the d-band electrons, the assignments made with the $\Delta\alpha$ formalism are very far from the correct values; see Table 2. The poorest results are obtained with the dd_{deloc} final double-hole state. The Wagner Auger parameter predictions are that, when the lattice is contracted, there is an increase in E_R that is ~50% larger than the increase in the BE, ΔBE(ΔSCF); similarly, when the lattice is expanded, the predicted decrease of E_R is greater than the decrease of ΔBE(ΔSCF). These large values for ΔE_R lead to values of ΔBE(Initial) that also have an unusually large magnitude. While E_R depends weakly on the metal NN distances, see Table 1; the large dependence obtained with the Wagner Auger parameter analysis is not physically reasonable. This incorrect behavior is not surprising since the Auger double hole is in a delocalized orbital rather than a localized orbital and it is not expected that the assumptions of the Wagner analysis will hold for delocalized double-hole Auger final states [1,6,8–10]. When we turn to the dd_{loc} final state, the Wagner Auger parameter analysis decomposition of the ΔBE is still rather poor and misleading. For example, for the contraction to $r(NN) = 5.16$ bohr, the $\Delta\alpha$ analysis gives an increase of the final state relaxation that is an order of magnitude larger than obtained by the exact WF analysis. In turn, this incorrect overestimate of ΔE_R leads to a ΔBE(Initial) that is 50% too large. In other words, the localization of the d-hole is not as extreme as expected [11,12] and the Ag 4d level cannot be considered as an atomic core level. When we use a true $CC'C''$ Auger transition with $M_{4,5}N_1N_1$, the $\Delta\alpha$ analysis resembles the correct decomposition. Although the magnitude of ΔE_R is still somewhat too large, see Table 2, it is small and the initial state effects are properly shown to be ΔBE(ΔSCF) ≈ ΔBE(Initial). It is only when we use the $\Delta\beta$ formalism that a correct decomposition into initial and final state shifts is obtained. In particular, the $\Delta\beta$ analysis correctly reproduces the dominant initial state character of the BE shifts due to lattice strain; the magnitude of the errors obtained with this analysis are consistently $\leqslant 0.03$ eV.

Our results with the $M_{4,5}dd_{loc}$ and $M_{4,5}dd_{deloc}$ Auger transitions for Ag_{13} are not consistent with the decompositions obtained either by Luo et al. [12] for the growth of Ag particles or by Wu et al. [11] for the growth of Cu particles. Of course, while we have focused entirely on lattice strain, measurements of the BE shifts for supported particles reflect both the effects of lattice strain and of particle size growth. Thus, our calculations will not reproduce [4] the shape of the experimental curves with particle size obtained using the Wagner Auger parameter with (Core, dd) Auger transitions. Furthermore, while we have considered only two particular dd hole states for the Auger process, the experiment will sum over the energies of all possible final double hole states in the d band weighted by the Auger intensities for these final states. However, we have shown that the Auger parameter analysis with $(n-1)$d-hole Auger final states is not able to correctly decompose the BE shifts arising from lattice strain into initial and final state contributions. We have also shown that when Auger transitions involving holes entirely in core-levels, $(C, C'C'')$, are used, both the $\Delta\alpha$ and $\Delta\beta$ Auger parameter formulations correctly show that the BE shifts arising from lattice strain are dominantly due to initial state effects. In particular, the errors in the decomposition of the $\Delta\beta$ analysis are quite small.

The present work demonstrating the role of lattice strain for the BE shifts of supported metal particles extends and enhances a previous combined theoretical and experimental study [4] of the BE shifts of supported 3d transition metal particles. This work had shown that initial state effects account for a significant portion of the BE shift with increasing particle size. The present work shows that the Wagner Auger parameter analysis using $(n-1)$d hole final Auger states is not able to decompose the BE shifts due to lattice strain into initial and final state contributions. It presents a challenge to experiment to find suitable $(C, C'C')$ Auger transitions so that the modified $\Delta\beta$ Auger

parameter formalism [10] can be used to correctly separate initial and final state contributions to the ΔBE of supported metal particles. In particular, such studies could provide definitive information about the role of lattice strain in small nano-particles in contributing to these BE shifts. While the desired one- and two-hole states may not be available in the laboratory, they are accessible with synchrotron radiation [20].

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