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# Separating ground state and screening contributions to chemical shifts

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**Abstract.** A recently developed potential model is used to derive expressions for the chemical shifts measured by electron spectroscopy. The accuracy and reliability with which the initial state charge and core hole screening charge can be determined from experimental chemical shifts are discussed. The model is applied to the free-atom to metal shifts of Na, Mg and Zn. It predicts appropriate values of the valence charges and indicates perfect local screening of core holes in the metallic phase of these elements.

## 1. Introduction

It is well known that shifts in core level photoelectron binding energies  $E_b$  and core–core–core Auger kinetic energies  $E_k$  for an atom in different chemical environments reflect differences in both the ground state core potential  $V$ , due to changes in the local charge distribution, and final state relaxation energies  $R$ . We may write [1]

$$\Delta E_b = \Delta V - \Delta R \quad (1a)$$

$$\Delta E_k \approx -\Delta V + 3\Delta R. \quad (1b)$$

By exploiting the difference in scaling with the number of core holes we may separate  $\Delta V$  and  $\Delta R$  by defining  $\beta$  and  $\xi$  :

$$\Delta\beta(ijj) \equiv \Delta E_k(ijj) + \Delta E_b(i) + 2\Delta E_b(j) \approx 2\Delta V \quad (2a)$$

$$\Delta\xi(ijj) \equiv \Delta E_k(ijj) - \Delta E_b(i) + 2\Delta E_b(j) \approx 2\Delta R \quad (2b)$$

referred to as initial state and final state Auger parameters (APs) respectively [1, 2, 3].  $\Delta\xi$  gives insight into the final state effects of polarization, relaxation and screening [4], while potential shifts are often interpreted in terms of ground state charge transfer [5, 6]. The separation of initial and final state effects is receiving renewed interest, particularly with regard to understanding the bonding at surfaces and interfaces [3, 7, 8].

We have recently [9] developed a potential model treatment of chemical shifts, in which the potential parameter  $k$ , relating potential shifts to charge state, has an explicit dependence on the valence charge  $q$  and core occupancy  $N$ . This earlier work [9] focused on the understanding of the metal to atom final state AP shifts of Na, Mg and Zn and the role of extra-atomic screening in the metallic phase. In the present work we assess the extent to which the extended potential model correctly describes ground state charges by analysing the corresponding initial state AP shifts of the elements studied previously. Simultaneous analysis of initial and final state AP shifts (or XPS and Auger shifts) with the potential model yields an empirical determination of both  $q$  and the core hole screening charge  $dq/dN$ .

## 2. Charge transfer and the potential model

A simple ground state potential model was developed by Seigbahn and co-workers [5, 6] in which XPS shifts are related to charge transfer by the expression

$$\Delta E_b \approx \Delta V = \Delta V^{\text{valence}} + \Delta V^{\text{ea}} = \Delta q \left( k - \sum_i \frac{1}{R_i} \right) \quad (3)$$

where  $V^{\text{valence}}$ , the potential experienced by a core electron on account of the valence charge, is assumed to be proportional to  $\Delta q$ , and  $V^{\text{ea}}$ , the extra-atomic contribution, is given here within the point charge approximation as the Madelung potential. Although chemical shifts are still often interpreted solely in terms of initial state effects, Thomas has shown [10] that the potential model can be generalized to cope explicitly with relaxation. By expanding the total energies of core hole states as Taylor series in core occupancy  $N$  [2, 11], Thomas [10] expressed one- and two-hole binding energies as

$$E_b(j) = V - \frac{1}{2} \left( \frac{\partial V}{\partial N} \right)_{N=0} + \frac{1}{6} \left( \frac{\partial^2 V}{\partial N^2} \right)_{N=0} - \dots \quad (4a)$$

$$E_b(jj) = 2V - 2 \left( \frac{\partial V}{\partial N} \right)_{N=0} + \frac{4}{3} \left( \frac{\partial^2 V}{\partial N^2} \right)_{N=0} - \dots \quad (4b)$$

respectively, where we define [9] the ground state to be  $N = 0$ .

It has been shown [9, 12, 13] that  $V^{\text{valence}}$  is better described by

$$V_{\text{nl}}^{\text{valence}}(N_{\text{nl}}, q) = \int_0^q k(N_{\text{nl}}, q') dq' \quad (5)$$

where the 'constant' of proportionality  $k$  in equation (3) is now given by

$$k(N_{\text{nl}}, q) = a + Nb + qd \quad (6)$$

with  $a$ ,  $b$  and  $d$  determined from the results of atomic structure calculations [14, 9]. This expression allows straightforward determination of the derivatives in equation (4), and is easily generalized to include higher-order terms. The coefficients  $c$  and  $e$  of the next order terms are found to be [9] an order of magnitude smaller than  $b$  and  $d$ . Using equations (4)–(6), and assuming linearity of  $q$  and  $V^{\text{ea}}$  in  $N$ , we have obtained [9] the expression

$$\Delta \xi = \Delta \left\{ qb + \frac{dq}{dN} \left[ a - 2b + d \left( q - \frac{dq}{dN} \right) \right] + \frac{dV^{\text{ea}}}{dN} \right\} \quad (7)$$

for the final state AP shift for two chemical environments of an atom.

$\xi$  is a reference-free quantity, independent of the specimen work function and charging effects, and so the experimental error in determining  $\Delta \xi$  is often smaller than in measuring  $\Delta E_b$  or  $\Delta E_K$ . This cancellation of errors does not occur for the initial state AP [14, 3, 8]. There are, however, a number of important cases where the error in  $\Delta \beta$  is small. In the measurement of gas phase electron spectra, for example, uncertainties in work functions do not occur and calibration is facilitated by mixing a noble gas with the sample gas. Calibration and referencing errors in chemical shifts between environments also cancel when both species are present in the same spectrum. This applies to the measurement of shifts between bulk and interface layers. In such cases  $\Delta \beta$  can be accurately measured and merits detailed analysis.

Consequently, we have derived similar expressions to equation (7) for  $\Delta E_b(j)$ ,  $\Delta E_k(ijj)$  and  $\Delta\beta(ijj)$ , all of the form

$$\Delta X = \Delta \sum_{n=0}^2 c_n \left( \frac{\partial^n V}{\partial N^n} \right) \quad (8)$$

where the coefficients  $c_n$  are obtained by Taylor expansion of total energies. We obtain

$$\Delta\beta = \Delta \left\{ 2aq + dq^2 - \frac{2}{3} \frac{dq}{dN} \left[ 2b + d \frac{dq}{dN} \right] + 2V^{ea} \right\} \quad (9a)$$

$$\Delta E_b = \Delta \left\{ \left( a - \frac{b}{2} \right) q + \frac{d}{2} q^2 + \frac{dq}{dN} \left[ \frac{b}{3} - \frac{a}{2} + d \frac{dq}{dN} \left( \frac{1}{6} - \frac{q}{2} \right) \right] + V^{ea} - \frac{1}{2} \frac{dV^{ea}}{dN} \right\} \quad (9b)$$

$$\Delta E_k = \Delta \left\{ \left( \frac{3b}{2} - a \right) q - \frac{d}{2} q^2 + \frac{dq}{dN} \left[ \frac{3a}{2} - \frac{7b}{3} + d \frac{dq}{dN} \left( \frac{3q}{2} - \frac{7}{6} \right) \right] - V^{ea} + \frac{3}{2} \frac{dV^{ea}}{dN} \right\}. \quad (9c)$$

It should be noted that  $\Delta E_k(ijj)$  and  $\Delta\beta(ijj)$  are functions of two core orbitals, and the sensitivity of core level shifts to changes in the valence charge distribution increases slightly with the localization of the core level, i.e.  $k$  has a weak orbital dependence [9]. For clarity we have chosen here to adopt the approximation that the response of all core levels to the chemical environment is the same and we drop the orbital dependence of  $k$ .

According to equations (7) and (9), the shifts  $\Delta E_b$ ,  $\Delta E_k$ ,  $\Delta\xi$  and  $\Delta\beta$  are each determined by both  $q$  and  $dq/dN$ . Selection of any two of these equations gives a closed system from which a graphical separation of initial and final state effects can be made. Solution curves ( $q, dq/dN$ ) consistent with the calculated values of  $k(N, q)$  and experimental values of  $\Delta E_b$ ,  $\Delta E_k$ ,  $\Delta\xi$  and  $\Delta\beta$  can be generated, with the intersection of these curves providing an empirical determination of the ground state charge transfer and core hole screening. This graphical approach makes the sensitivity of the chemical shifts to  $q$  and  $dq/dN$  explicit.

It is more usual to use  $\Delta\xi$  to estimate  $\Delta R$  according to  $\Delta\xi = 2\Delta R - \Delta E_{\text{correction}}$  [10] allowing isolation of  $\Delta V$  from  $\Delta E_b$ . With the potential model in equations (5)–(6) we obtain

$$\Delta\xi = 2\Delta R - \Delta \left\{ \frac{2}{3} \frac{dq}{dN} \left[ 2b + d \frac{dq}{dN} \right] \right\} \quad (10)$$

which simplifies to the expression derived by Thomas [10] if we set  $d = 0$ . Since  $|b| \approx d$  it can be seen that neglect of  $d$  can lead to an overestimate of  $E_{\text{correction}}$  by a factor of  $\approx 2$ .

We now apply the graphical procedure to the metal-atom shifts of Na, Mg and Zn. As pointed out by Johansson and Mårtensson [15] there is some scatter in the quoted core level binding energies, Auger energies and work functions of metals. In general then the study of metal-atom shifts is not expected to be a favourable case from the point of view of error cancellation. However the study of two phases of the same element provides a good test of the validity of the potential model and the reliability with which  $q$  and  $dq/dN$  can be determined from measured chemical shifts since the valence charges are known exactly.

### 3. Metal-atom shifts

It has previously been shown [14] that a single function  $k(N, q_{\text{sp}})$  can be used for systems with only s and p character valence charge, while d charge must be treated separately. For

simplicity we only consider sp systems in the present work. XPS and Auger shifts between metallic and free-atom Na, Mg and Zn are shown in table 1, and have been combined to give AP shifts. Atomic potential parameters for Mg, Zn and Na, calculated using the Dirac-Fock code of Desclaux [17] are also given in table 1. It is well known that the valence wavefunctions are compressed when an atom is embedded in a solid. This is usually accounted for [16, 14] by renormalizing  $V^{\text{valence}}$  by a factor  $\gamma$ , where  $\gamma \gtrsim 1$ . Solution sets of  $q$  against  $dq/dN$  consistent with the metal to free-atom AP shifts for Na, Mg and Zn are shown in figure 1, where we have taken  $\gamma = 1$  in each case. We find empirical valence charges for Na, Mg and Zn metals of  $-1.11$ ,  $-2.11$  and  $-1.84$  respectively (table 1) in reasonable agreement with their true values. The experimental errors correspond to  $\approx 0.1$  in  $q$ , and  $\approx 0.05$  in  $dq/dN$ , while the neglect of the orbital dependence of  $k$  should contribute somewhat smaller errors. Corresponding values of  $dq/dN$  are 1.04, 1.03 and 1.06 respectively. Considering now the effect of varying  $\gamma$ , we find that  $\gamma_{\text{Mg}} = 1.05$  yields  $q = -1.95$  and  $dq/dN = 0.95$ , while  $\gamma_{\text{Mg}} = 1.1$  yields  $q = -1.84$  and  $dq/dN = 0.88$ .

A phase parameter  $\phi$  associated with the relative uncertainty in  $q$  and  $dq/dN$  inherent in each experimental shift can be defined by the gradient of the solution curve, i.e.  $\phi = \tan^{-1} \{ \delta q / \delta (dq/dN) \}$ , in the vicinity of the intersection. These are largely determined by the coefficients  $c_n$  and  $k(N, q)$  for a given element. Values of  $\phi$  for Mg are shown in table 2 and are very similar for the three elements studied here.

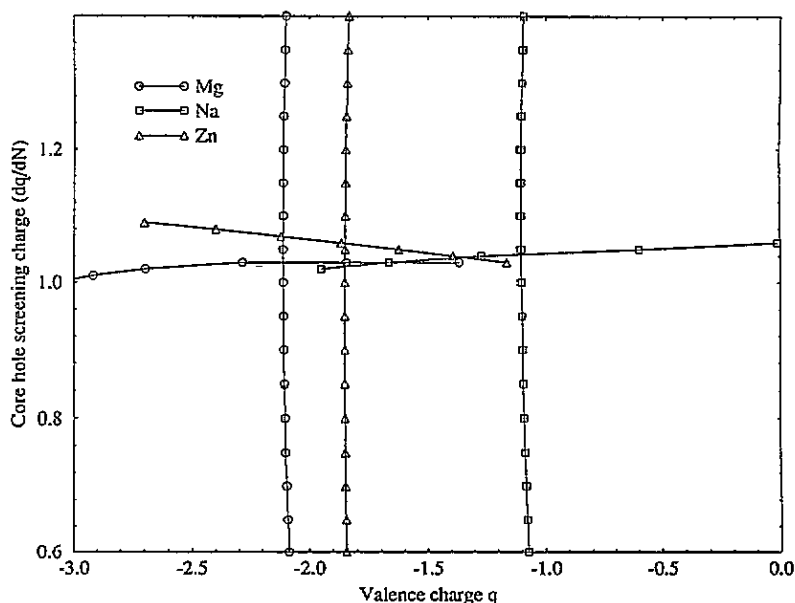


Figure 1. Solution curves ( $q, dq/dN$ ) consistent with experimental metal-atom final state AP shifts (horizontal curves) and the initial state AP shifts (vertical curves).

Given the stated experimental error, the empirical solid state valence charges given in table 1 are in reasonable agreement with known corresponding Wigner-Seitz charges. Having noted the basic soundness of the potential model description of metal-atom shifts we now consider the results in detail in terms of the solid state modifications to the calculated values of  $k$ .

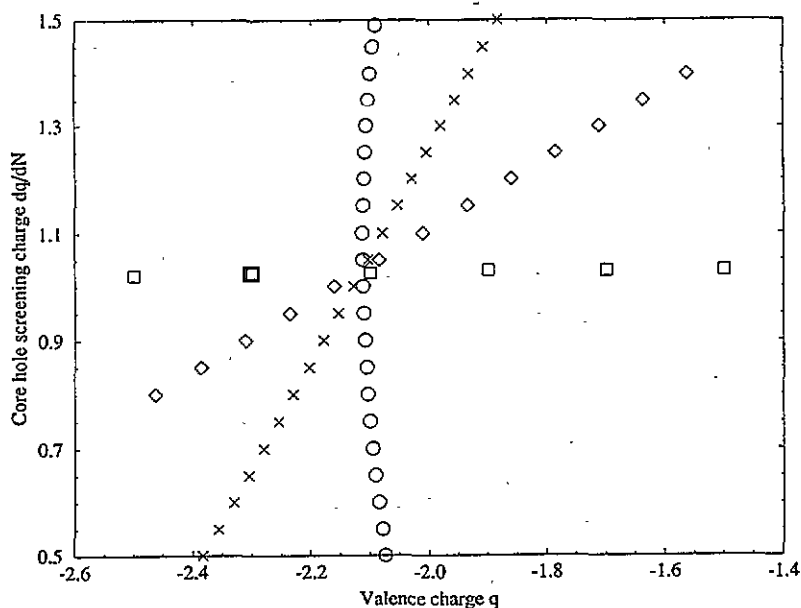


Figure 2. Solution curves ( $q$ ,  $dq/dN$ ) consistent with the experimental metal-atom one-hole binding energy shift  $\Delta E_b(j)$  (crosses), Auger shift  $\Delta E_k$  (diamonds), initial state AP shift  $\Delta\beta$  (circles), and final state AP shift  $\Delta\xi$  (squares) for Mg.

Table 1. Metal-atom shifts (in eV) for Na, Mg and Zn from the data compiled by Aksela *et al* [19]. Estimated errors in  $\Delta E_b$  and  $\Delta E_k$  are 0.5 eV. Also shown are calculated parameters  $a$ ,  $b$  and  $d$  for these elements, and empirically deduced values of  $q$  and  $dq/dN$  for the metals.

	Na	Mg	Zn
$\Delta E_b$	-4.6	-4.8	-3.1
$\Delta E_k$	14.3	15.0	13.1
$\Delta\xi$	9.7	10.2	10.0
$\Delta\beta$	0.5	0.6	3.8
$a$	8.81	13.0	12.8
$b$	-2.91	-2.24	-1.50
$d$	2.35	2.91	2.50
$q$	-1.11	-2.11	-1.84
$dq/dN$	1.04	1.03	1.06

Table 2. Phase angles  $\phi$  for the metal-atom chemical shifts of Mg.

	$\phi$
$\Delta E_b$	$63^\circ$
$\Delta E_k$	$35^\circ$
$\Delta\xi$	$-1^\circ$
$\Delta\beta$	$91^\circ$

#### 4. Discussion

The increase in electronegativity across the periodic table suggests that, if the equivalent cores approximation provides an accurate description of the local electronic structure of a

core ionized site in a simple metal, there will be a slight 'over-screening' of core holes, consistent with the values of  $dq/dN$  in table 1 which exceed unity. However we have found that small increases of  $\gamma$  above 1 tend to reduce our empirical values of  $dq/dN$ . The question as to the appropriate value of  $\gamma$  is therefore of interest. As noted in the previous section, the effect of condensing free-atoms into the solid phase involves compression of the valence wavefunctions leading to an effective increase in  $k$  [16, 14]. It is also well known that comparisons of calculated charge densities for metals with superpositions of atomic charge densities indicate a transfer of density from the atomic spheres to the interstitial regions. This delocalizing effect would tend to reduce  $k$ . To investigate the relative magnitudes of these opposing effects we can turn the problem round and take the known solid state valence charges and the perfect screening assumption ( $dq/dN = 1$ ) and use the potential model to calculate metal-atom XPS, Auger and AP shifts. Values of these calculated quantities are shown in table 3 for Na, Mg and Zn. Scaling  $V^{\text{valence}}$  so as to reproduce the experimental metal-atom shifts gives the values of  $\gamma$  shown in table 3. We find that  $\gamma_{\text{Na}} \approx 1.06$  and  $\gamma_{\text{Mg}} \approx 1.03$  provide consistency between the potential model parameters, the local charge, the perfect screening model and experimental metal atom shifts. For Na and Mg we conclude that the solid state gives rise to a slight enhancement of  $k$ .

Table 3.  $\Delta E_b$ ,  $\Delta E_k$ ,  $\Delta\beta$  and  $\Delta\xi$  calculated metal atom shifts (in eV) for Na, Mg and Zn. Corresponding values of  $\gamma$  determined by the discrepancy between calculated and experimental shifts are also shown.

	$\Delta E_b$		$\Delta E_k$		$\Delta\xi$		$\Delta\beta$	
	Calc	$\gamma_{\text{emp}}$	Calc	$\gamma_{\text{emp}}$	Calc	$\gamma_{\text{emp}}$	Calc	$\gamma_{\text{emp}}$
Na	-3.8	1.06	13.2	1.05	9.7	1.03	1.8	1.10
Mg	-4.0	1.03	13.9	1.03	9.9	1.02	1.8	1.03
Zn	-4.2	0.96	13.7	0.98	9.5	1.04	1.2	0.93

The situation appears to be more complicated for Zn where large discrepancies between the calculated and experimental shifts are observed for all quantities except  $\Delta\xi$ . This difference between Zn and the simple metals may be understood in terms of what is expected to happen to the Zn 3d levels in the metal. Any delocalization of the 3d states will give rise to a more attractive core potential in the metal and hence an additional  $\Delta V$  contribution to  $\Delta E_b$ ,  $\Delta E_k$  and  $\Delta\beta$ . Since  $c_0(\xi) = 0$  and the Zn 3d band is filled in the metal, the final state AP shift is only sensitive to the solid state effects on the sp states, and  $\gamma_{\text{Zn}} = 1.04$  derived from  $\Delta\xi$  is therefore in keeping with  $\gamma_{\text{Na}}$  and  $\gamma_{\text{Mg}}$ . The delocalization of the d band states may give rise to the relatively small metal-atom XPS shifts [19] of all the group IB and IIB elements where the valence d states are filled, and so do not play a role in extra-atomic screening, but are involved in the bonding.

We find  $\phi(\xi) \approx 0^\circ$  and  $\phi(\beta) \approx 90^\circ$  and hence the charge and screening dependencies of the AP shifts are largely decoupled. This means that values of  $\Delta q$  ( $\Delta dq/dN$ ) deduced solely on the basis of  $\Delta\xi$  ( $\Delta\beta$ ) will be extremely sensitive to the choice of  $dq/dN(q)$ . Banna, Slaughter and Matthews [13] have argued that reasonable estimates of  $q$  and  $dq/dN$  can be obtained using Pauling's [18] relation of fractional ionic character to electronegativity difference. If only  $E_b$  or  $E_k$  can be obtained, it may be useful to estimate either  $q$  or  $dq/dN$  as described by Banna *et al* [13] and use  $\phi$  to place limits on the other parameter.

The success of the potential model described by equations (5)–(6) in correctly describing the one- and two-core hole excitation energies of metals and atoms suggests that the essential

bonding properties of the elements and their variation with core ionization and valence charge are well described by the model parameter  $k(N, q)$ . In equation (6),  $b$  represents the collapse of valence levels towards core holes, while  $d$  represents the increased/reduced effective nuclear potential on removal/addition of valence charge. Solid state effects are included via the appropriate Madelung potentials and the screening charge  $dq/dN$ , treated here as a parameter to be empirically determined, as well as minor modifications to  $k$ . Non-linear screening effects, whereby the screening charge at a doubly core ionized site is less than twice that at a one-hole site, are also readily incorporated into the model, and may be important in molecules.

Saethre *et al* [12] have recently investigated the validity of the point charge approximation for molecular charge distributions. These authors found that analysis of core potential shifts within the point charge model gave rise to modest underestimates of charge transfer. Indeed they found that for molecules of low-polarity  $V^{ea}$  could be dominated by higher multipoles of the charge distribution. While the consequence of the non-spherical charge distribution in molecules leads to an underestimate of  $q$ , the renormalizing factor  $\gamma$  would have the opposite effect. Clearly, application of the potential model will be most reliable for comparison of similar systems where systematic errors due to the simplifying assumptions may largely cancel.

## 5. Summary

The role of initial and final state contributions to chemical shifts observed in electron spectra has been discussed. Following the procedure of Thomas [10], we have derived the relation between the ground state charge transfer, core hole screening and the initial state AP, using a recently extended [9] potential model. The necessary parameters can be calculated from first principles and have clear physical meaning. We have compared solution sets ( $q, dq/dN$ ) for  $\Delta\xi, \Delta\beta, \Delta E_b, \Delta E_k$  for Na, Mg and Zn, metal-atom shifts and characterized the precision to which  $q$  and  $dq/dN$  can be determined from each quantity in terms of a phase angle. The intersection of the solution curves provides an empirical determination of  $q$  and  $dq/dN$ . In all cases the empirical valence charges are in reasonable agreement with their true values for the elements studied here (to within  $\approx 0.1$ ). For the metallic phase of these elements we find that  $dq/dN \approx 1.0$  implying perfect local screening of core holes. The fact that the  $k$  functions calculated for free-atoms are also quite appropriate for the metallic phase relies on the near cancellation of opposing solid state effects of the delocalization of charge from the atomic sites and the compression of charge within the Wigner-Seitz cell. We find that sp valence states lead to a slight net enhancement of  $k$  in the metallic phase, while the d band of Zn had the opposite effect.

The description of chemical bonding in terms of the scalar quantity referred to as the 'atomic' or local charge is a crude approach. However, the chemical concepts of charge transfer and oxidation state have proved very powerful in understanding a range of physical and electronic properties of solids. We suggest that the potential model approach could be particularly useful for investigating interface systems where bulk and interface signals are detected simultaneously and the error in  $\Delta\beta$  is therefore small.

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