

Core-Level Binding-Energy Shifts in Metals

A. R. Williams and N. D. Lang

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 7 November 1977)

We describe a theory of core-level binding-energy shifts in metals (relative to the free atom). Precise definitions of the intuitive concepts of chemical, relaxation, and configuration shifts are given which permit their straightforward and unambiguous evaluation. Parameter-free calculations for the $3d$ transition series agree well with experiment. The simplicity of the theory should make it widely applicable.

The measurement of core-level energies by x-ray photoemission is one of the most important available probes of electronic structure. Such binding energies are of interest because they reflect (via the electrostatic potential in the atomic core region) the chemical environment of the atom from which the core electron is removed. We focus here on the shift of core-level binding energies associated with the formation of a metal from free atoms. We present a theory in which all significant contributions to the shift are accurately calculated and identified with intuitively understandable concepts. The same problem has been considered previously by Ley *et al.*,¹ by Watson, Perlman, and Herbst,² and, most recently, by Shirley *et al.*³ The total shift Δ is the difference of two binding energies,

$$\Delta \equiv \{E^A(n_c - 1) - E^A(n_c)\} - \{E^S(n_c - 1) - E^S(n_c)\}, \quad (1)$$

where $E(n_c)$ is the total energy of the system considered as a function of the number of electrons in a particular core level. The superscripts A and S indicate that the first bracketed quantity is the core-level binding energy for the free atom and the second bracketed quantity is that for the solid. We decompose the total shift into contributions due to configuration changes,² chemical shifts,⁴ and relaxation shifts^{1,2,4}:

$$\Delta = \Delta_{\text{config}} + \Delta_{\text{chem}} + \Delta_{\text{relax}}. \quad (2)$$

We define Δ_{config} to be the change in the core-level binding energy due only to changing the configuration (the distribution of electrons among s , p , and d states) of the free atom (denoted by A) into a configuration similar to that which the atom will adopt in the solid⁵ (denoted by A^*):

$$\Delta_{\text{config}} \equiv \{E^A(n_c - 1) - E^A(n_c)\} - \{E^{A^*}(n_c - 1) - E^{A^*}(n_c)\}. \quad (3)$$

To evaluate the remaining two contributions, Δ_{chem} and Δ_{relax} , we take the total energy to be

an analytic function of core occupation and express the contributing binding energies as Taylor series:

$$E(n_c - \delta n_c) - E(n_c) = -\frac{\partial E}{\partial n_c} \delta n_c + \frac{1}{2} \frac{\partial^2 E}{\partial n_c^2} (\delta n_c)^2 - \dots \quad (4)$$

with $\delta n_c = +1$. The convergence of such series has been studied by Slater.⁶ In the density-functional formalism,⁷ which we use to evaluate the quantities required by the analysis, partial derivatives of the total energy with respect to occupation are rigorously given by the orbital eigenenergies; in particular, $\partial E/\partial n_c = \epsilon_c$. When this fact is used in the Taylor-series representation of the binding energy [Eq. (4)], term-by-term subtraction of the series representing $E^S(n_c - 1) - E^S(n_c)$ from that representing $E^{A^*}(n_c - 1) - E^{A^*}(n_c)$ leads to natural definitions of the chemical and relaxation shifts,

$$\Delta_{\text{chem}} \equiv \epsilon_c^S - \epsilon_c^{A^*} \quad (5)$$

and

$$\Delta_{\text{relax}} = -\frac{1}{2} (\partial \epsilon_c^S / \partial n_c - \partial \epsilon_c^{A^*} / \partial n_c) + \dots \quad (6)$$

The chemical shift⁸ is the displacement of the core level by changes in the chemical environment *before* an electron is removed from the level. The remaining terms in the Taylor series [Eq. (6)] describe the shift of the level caused by removal of the electron and are therefore to be identified with relaxation.⁹

While our expressions for Δ_{config} and Δ_{chem} require for their evaluation only relatively straightforward free-atom and energy-band calculations,⁵ the evaluation of Δ_{relax} [Eq. (6)] is much more complicated, because the quantity $\partial \epsilon_c^S / \partial n_c$ refers to an infinite solid in which the translational symmetry required for band calculations is broken by the presence of a localized core hole. It is here that we make use of the excited-atom model,^{1,2,10} according to which the relaxation-induced

displacement of the core level in the solid, $\epsilon_c^S(n_c - \delta n_c) - \epsilon_c^S(n_c)$, can be approximated by that of a core level in a free atom whose neutrality is maintained by "exciting" the core charge δn_c into a valence orbital, i.e.,

$$\begin{aligned} \epsilon_c^S(n_c - \delta n_c) - \epsilon_c^S(n_c) \\ \approx \epsilon_c^{A^*}(n_c - \delta n_c, n_v + \delta n_c) - \epsilon_c^{A^*}(n_c, n_v), \quad (7) \end{aligned}$$

where n_v is the occupation of the valence orbital. The motivation for this approximation is that metallic screening preserves local neutrality and furthermore that the spatial distribution of the metallic screening charge is accurately approximated by self-consistently adding an extra electron to the valence shell.^{2,10} When the excited-atom approximation [Eq. (7)] is used to describe the n_c dependence of ϵ_c^S in our expression for the relaxation shift [Eq. (6)], we obtain¹¹

$$\Delta_{\text{relax}} \approx \frac{1}{2}(\partial \epsilon_c^{A^*} / \partial n_v). \quad (8)$$

As in the analysis leading to Slater's transition-state technique,⁶ Taylor-series terms of higher (than lowest contributing) order can be included by evaluating quantities at intermediate-level occupations. In the present case, terms of order $(\delta n_c)^3$ are accounted for by evaluating the derivative $\partial \epsilon_c^{A^*} / \partial n_v$ appearing in Eq. (8) at an occupation consisting of two thirds of a core hole and one third of a screening (extra valence) electron. One- and two-thirds occupations arise because we are combining second- and third-order terms, whose relative weighting in Taylor series, such as Eq. (4), is one-third [e.g., $\epsilon'(n) + \frac{1}{3}\epsilon''(n) \approx \epsilon'(n + \frac{1}{3})$].

The numerical results corresponding to the preceding analysis are compared with experimental measurements in Fig. 1.¹² The configuration shift Δ_{config} was evaluated using Eq. (3), Δ_{chem} using Eq. (5), and Δ_{relax} using Eq. (8). All the required atomic and energy-band calculations were self-consistent and paramagnetic, and used the local-density approximation⁷ to exchange and correlation effects. (The Fermi energy, and thus all energies arising in the energy-band calculations, were referenced to vacuum using measured work functions.¹³) Figure 1 shows that the principal variation of the total shift with atomic number stems from configuration changes.² The relaxation shift, while large, is slowly varying. The breaks in the relaxation curve at Ca and Ni reflect changes in the character (*s* vs *d*) of the screening electron; the latter was deduced from the solid configurations A^* using the "equivalent-

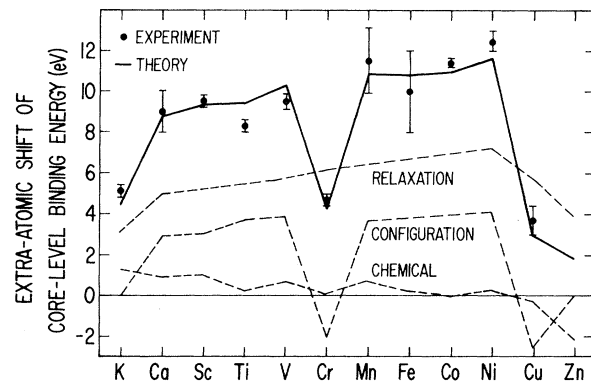


FIG. 1. Comparison of calculated and measured (see Ref. 12) binding-energy shifts for 3d transition series and decomposition of total calculated shift into contributions due to chemical, configuration, and relaxation effects.

core" concept¹⁴: For the transition metals, e.g., the screening charge is *d*-like.¹⁵ Note that, since the free-atom binding energy corresponding to A^* is added and subtracted, the total shift would be completely independent of A^* , were it not for our use of the excited-atom approximation. In Ni, for example, changing A^* from $3d^{8.6}4s^{1.4}$ to $3d^{8.7}4s^{1.3}$ changes the total shift less than 0.07 eV. A similar change ($0.1e^-$) in the character of the screening electron changes Δ_{relax} by just 0.3 eV. Our calculated chemical shifts indicate the near cancellation of two larger effects, the downward shift due to the surface dipole-layer potential and the upward shift due to the compression of the valence charge into the smaller volume that it occupies in the solid; both of these effects are typically 2–5 eV in magnitude.

Our Taylor-series analysis provides an immediate clarification of a confusion which exists in the literature between the relaxation shift Δ_{relax} and a quantity Δ_s introduced in Ref. 2 and referred to as a screening energy. Hoogewijs, Fiermans, and Vennik¹⁶ noted the distinction between Δ_s and Δ_{relax} , but did not elucidate its origin; Taylor-series analysis makes it clear that Δ_s and Δ_{relax} are simply not the same type of physical quantity. Since it is a total-energy difference, $\Delta_s \equiv E^{A^*}(n_c - 1, n_v) - E^{A^*}(n_c - 1, n_v + 1)$ is fundamentally an *energy level* ($\Delta_s = -\epsilon_v^{A^*} + \dots$), whereas Δ_{relax} is an *energy-level shift* ($\Delta_{\text{relax}} = \frac{1}{2}\partial \epsilon_c^{A^*} / \partial n_v + \dots$). Numerically, Δ_s and Δ_{relax} differ both in their magnitude and in their dependence on the spatial character of the screening charge (3*d* vs 4*s*). The relaxation shift is generally smaller¹⁷ than Δ_s and, unlike Δ_s , which is

insensitive to the $3d$ vs $4s$ screening-charge distinction,² the relaxation shift Δ_{relax} , since it is essentially half the electrostatic potential in the core due to the screening charge,^{10,18} is larger for the spatially more localized third-shell electrons. (In the case of Ni, e.g., the relaxation shift due to screening by a d electron is 7.3 eV, whereas for screening by an s electron it would be only 4.5 eV.)

The Taylor-series analysis can also be used to represent Δ_{relax} in terms of total-energy differences, which can be obtained from measured free-atom excitation spectra using the equivalent-core approximation¹⁴ or calculated using any of a variety of techniques (including Hartree-Fock, e.g.). As the preceding paragraph indicates, however, Δ_{relax} , since it is an energy-level shift, must be represented by a *difference* of total-energy differences; we find for example that

$$\Delta_{\text{relax}} \approx \frac{1}{2} \{I_1(Z+1) - I_0(Z)\}, \quad (9)$$

where $I_0(Z)$ is the electron affinity of the atom in question and $I_1(Z+1)$ is the first ionization potential of the next atom in the periodic table. Another estimate of Δ_{relax} , which differs from Eq. (9) only in terms of order $(\delta n)^3$, is given by

$$\Delta_{\text{relax}} \approx \frac{1}{2} \{I_2(Z+1) - I_1(Z)\}, \quad (10)$$

where I_2 is the second ionization potential. Consideration of these third-order terms indicates that a linear combination consisting of two-thirds Eq. (9) and one-third Eq. (10) is more accurate than either taken by itself.¹⁹ When this procedure is applied to potassium using measured ionization potentials, the result for Δ_{relax} is 3.1 eV,²⁰ compared with the value of 3.3 eV shown in Fig. 1. [The application of Eqs. (9) and (10) to transition metals is complicated by multiplet structure and configuration changes.]

Both the present work and our detailed study of the excited-atom model in the context of atomic chemisorption¹⁰ indicate that this very simple model can be quite accurate. Our results motivate, for example, the study of the analogous "excited-molecule" model to estimate relaxation shifts in the context of molecular chemisorption.

We gratefully acknowledge conversations with J. F. Janak, D. E. Eastman, K. C. Pandey, R. A. Pollak, and D. E. Jepsen, and lengthy discussions of this work with U. von Barth, C. D. Gelatt, Jr., F. Forstmann, and P. S. Bagus.

¹L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pol-

lak, and D. A. Shirley, Phys. Rev. B **8**, 2392 (1973).

²R. E. Watson, M. L. Perlman, and J. F. Herbst, Phys. Rev. B **13**, 2358 (1976).

³D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, Phys. Rev. B **15**, 544 (1977).

⁴P. Citrin and D. R. Hamann, Chem. Phys. Lett. **22**, 301 (1973), and Phys. Rev. B **10**, 4948 (1974).

⁵For the free-atom calculations leading to quantities labeled by A^* , all fourth-shell (non- d -like) valence electrons were taken to be s -like. The change in the number of d electrons with formation of the solid [K, 0.0; Ca, +0.5; Sc, +0.6; Ti, +0.7; V, +0.7; Cr, -0.4; Mn, +0.6; Fe, +0.6; Co, +0.6; Ni, +0.6; Cu, -0.4; Zn, 0.0] was obtained from self-consistent band calculations. The latter employed a formalism developed by J. Kubler, A. R. Williams, and C. D. Gelatt, Jr. (unpublished), which is similar to the "LMTO" (linear muffin-tin orbital) method [O. K. Andersen, Phys. Rev. B **12**, 3060 (1975)]; it closely approximates results obtained by V. L. Moruzzi, A. R. Williams, and J. F. Janak [Phys. Rev. B **15**, 2854 (1977)], but requires much less computation and provides a simple and unambiguous angular-momentum decomposition of the electron density through its 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.)

⁶J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

⁷P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965); L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

⁸Note that, while the density-functional eigenenergies ϵ differ in their interpretation from their Hartree-Fock counterparts, the eigenenergy difference $\epsilon_c^S - \epsilon_c^A$ is similar. In both cases (density functional and Hartree-Fock) this difference is basically the change in the electrostatic potential in the core region due to the valence-electron displacements associated with chemical bonding. See, e.g., U. Gelius, Phys. Scr. **9**, 133 (1974).

⁹Note that these terms in the individual series, which we have subtracted, contain common contributions describing the elimination of the self-interaction artificially introduced by the local-density approximation (see Ref. 6).

¹⁰N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1977).

¹¹The fact that the partial derivative $\partial \epsilon_c^S / \partial n_c$ includes the formation of the extra-atomic screening charge implies that the appropriate use of Eq. (7) in Eq. (6) is the following: $\partial \epsilon_c^S / \partial n_c \approx d \epsilon_c^A (n_c + n_v \text{ held constant}) / dn_c = \partial \epsilon_c^A / \partial n_c - \partial \epsilon_c^A / \partial n_v$.

¹²The experimental data is that compiled in Ref. 3 using theoretical estimates of the free-atom binding energy and measured work functions. To eliminate dependence of our calculated level shifts on the core

state involved ($1s$, $2s$, $2p$, etc.) we have replaced the variation of ϵ_c in Eqs. (5) and (8) with the variation of the electrostatic potential at the nucleus. (This is appropriate only for deep core levels.) We have compared our results with measurements on $2s$ levels, because we feel that the atomic calculations employed in Ref. 3 are less reliable for the $1s$ levels, and p levels introduce the complication of multiplet structure. The error bars in Fig. 1 reflect only the reported uncertainty associated with the measurement of the core-level binding energy in the solid; an estimate of the additional uncertainty introduced by the use in Ref. 3 of theoretical free-atom binding energies can be obtained from the errors in these binding energies for the rare-gas atoms, for which measurements are available. For Ne and Ar, the errors are less than 1 eV; for Kr, the error is large (8 eV). The only indication we have that the errors remain small through the $3d$ transition series is the empirical one offered by the uniform level of agreement that we obtain.

¹³We use the same work functions used to define the experimental data (see Ref. 12).

¹⁴Valence electrons are affected similarly by a core hole and an extra proton. See, e.g., D. A. Shirley, *Chem. Phys. Lett.* **16**, 220 (1972). Thus, the valence charge of a screened atom containing a core hole is similar to that of the next atom in the periodic table.

¹⁵The screening electron is s -like for K, p -like for

Zn, 60% s -like and 40% d -like for Cu, and purely d -like otherwise. [In using the equivalent-core approximation to specify the screening charge (see Ref. 14), we ignore the 0.5 d electrons in Ca and the 0.1 variation in the number of non- d electrons in Ti and V.]

¹⁶R. Hoogewijs, L. Fiermans, and J. Vennik, *Chem. Phys. Lett.* **37**, 87 (1976).

¹⁷In the equivalent-core approximation (see Ref. 14), $\Delta_s = I_1(Z + 1)$. Thus, Eq. (9), together with the fact that electron affinities are smaller than ionization potentials, indicates that Δ_s should be approximately twice Δ_{relax} . (See text below.)

¹⁸L. Hedin and A. Johansson, *J. Phys. B* **2**, 1336 (1969).

¹⁹This unequal weighting of formulas (9) and (10) is slightly more accurate than the equal weighting suggested in Ref. 10.

²⁰The corresponding result for the quantity Δ_s is 6.1 eV. If, as was done in Ref. 2, Δ_s is evaluated by the Hartree-Fock method, the result is 5 eV, regardless of whether the calculations are performed on Ca, or on K with a core hole. The general tendency of the Hartree-Fock method to underestimate such total-energy differences [see J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I, p. 392] reduces the numerical difference between Δ_s and Δ_{relax} , thereby obscuring the qualitative difference between the two quantities.

Polarization Phenomena in X-Ray Scattering

G. G. Cohen

Department of Physics and Astronomy, Vassar College, Poughkeepsie, New York 12601

and

M. Kuriyama

National Bureau of Standards, Washington, D. C. 20234

(Received 19 January 1978)

Rotation of the plane of polarization of a linearly polarized x-ray beam by simple transmission through a (110) silicon crystal has been observed. Both the amount of rotation and the amount of absorption of x rays depend on the orientation of the crystal in the incident beam. Contemporary scattering-theory calculations are used to explain this effect, including the x-ray analog to optical birefringence, for a suitable crystal sample.

In this Letter, we report the discovery of x-ray polarization rotation for the case of simple transmission. We have used linearly polarized Cu $K\alpha$ radiation incident perpendicular to the (110) surface of Si. Avoiding Bragg or Laue conditions, we demonstrate for the first time that there is a rotation of the linearly polarized x-ray beam and an absorption in the crystal sample which depend on the orientation of the Si

crystal.

Polarization phenomena such as optical activity and birefringence are not generally expected to exist for x rays in simple transmission. For the case of x-ray diffraction, however, theoretical results of Molière¹ and Ashkin and Kuriyama² indicate that the initial and final polarization states may be different. Hōjō, Ohtsuki, and Yanagawa³ have shown, however, that as long as