

Theory of *KLL* Auger Energies Including Static Relaxation*

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A previously overlooked relaxation energy R is introduced into the intermediate-coupling formulas of Asaad and Burhop to calculate the *KLL* Auger energies of the elements from $Z = 10$ to 100. By employing the concept of equivalent cores, together with the work of Hedin and Johansson on polarization energies of electron holes, a method was developed to estimate R accurately from ground-state two-electron integrals calculated by Mann. These integrals were also used in the intermediate-coupling calculation. Agreement with experiment is excellent. A table of *KLL* Auger energies based on this work is given. These energies appear to be preferable to the older semiempirical values because they are comparable in accuracy and they have a sound theoretical basis. Their adoption for analysis of Auger spectra is suggested. The semiempirical values were based on two sets of parameters for light and heavy elements. They gave good fits only by using unrealistic values of the two-electron integrals in the intermediate-coupling equations, because the relaxation energy was omitted. In addition to predicting *KLL* Auger energies accurately, this work shows that the spin-orbit coupling constant ζ for $2p$ electrons in two-hole states is essentially the same as in one-hole states. The success of the intermediate-coupling calculations also shows that two-electron integrals in these two-hole states are accurately equal to those calculated for neutral atoms. The relaxation-energy concept can be applied to other problems.

I. INTRODUCTION

In an Auger process an atom loses energy by a transition from an initial state possessing an inner-shell vacancy to a final state in which the inner vacancy is filled but two new vacancies are present further out. An electron is ejected in this transition. The Auger electron's kinetic energy is termed the "Auger energy" of the transition.

In this paper a theory is described that permits the prediction of $E(KLL)$, the *KLL* Auger energies of the elements, in terms of one-electron binding energies and two-electron Coulomb and exchange integrals. The application of this theory to KL_1L_1 energies alone was reported earlier.¹ In this paper the theory is described more thoroughly and applied to predict all nine *KLL* components. The key innovation in this work is the recognition of a previously overlooked "static" relaxation-energy term that has a considerable effect on $E(KLL)$. Inclusion of this term allows the accurate prediction of *KLL* Auger energies, without resorting to multi-parameter fits of experimental Auger energies. Theoretical values of $E(KLL)$ are derived and found to be in excellent agreement with experiment.

The earlier theory of Auger energies is briefly reviewed in Sec. II. The static relaxation energy is described in Sec. III. Calculation of the *KLL* Auger energies of the elements is described in Sec. IV, and the results are discussed in comparison with experiment in Sec. V.

II. EARLIER THEORY

Asaad and Burhop² made a major advance in the understanding of the *KLL* Auger spectrum by con-

sidering the effect of intermediate coupling in the two-hole final state. For the nine observable *KLL* lines they found expressions of the form

$$\begin{aligned} E(KL_1L_1; {}^1S) &= E(K) - 2E(L_1) - F^0(20, 20), \\ E(KL_2L_3; {}^1D) &= E(K) - E(L_2) - E(L_3) \\ &\quad - F^0(21, 21) + \frac{2}{25}F^2(21, 21) \\ &\quad + \frac{3}{4}\zeta - \left\{ \left[\frac{3}{25}F^2(21, 21) + \frac{1}{4}\zeta \right]^2 + \frac{1}{2}\zeta^2 \right\}^{1/2}, \end{aligned} \quad (1)$$

(and seven other equations).

The other seven equations are omitted here for brevity because our final equations [Eqs. (17)] are slightly modified forms of these equations. The notation in Eqs. (1) is standard. The final-state-term symbol is included in the expression for the Auger energy. One-electron binding energies are given as $E(K)$, etc. Two-electron integrals have their usual notation. Coulomb and exchange integrals will be denoted as J and K , respectively, while the component Slater integrals are denoted as F^k and G^k . The spin-orbit coupling constant is denoted as ζ . It can be obtained empirically from the empirical binding energies by using the relation $\zeta = 2[E(L_2) - E(L_3)]/3$. Asaad and Burhop estimated the two-electron integrals by fitting the data of Mladjenovic and Slätis³ for $Z = 83$, and assuming these integrals to vary as

$$F, G \sim A(Z - Z_s)(1 - \alpha Z^2), \quad (2)$$

where the $(1 - \alpha Z^2)$ term accounts for relativity. Later workers found difficulties with the form of Eq. (2). Hörnfeldt, Fahlman, and Nordling⁴ found it necessary to adjust A to fit new data, and Hörnfeldt⁵ found that a relativity term of the form

$(1 + \beta Z^3)$ gave a better fit. More recently Asaad⁶ derived a theoretical form $(1 + aZ^2)$ for this factor. A complete table of *KLL* Auger energies for $6 \leq Z \leq 104$ was compiled^{4,5,7} by fitting high-accuracy experimental Auger energies around $Z = 40$ to the Asaad-Burhop theory, using the term $(1 - \alpha Z^2)$ for $6 \leq Z \leq 40$ and $(1 + \beta Z^3)$ for $Z > 40$.

This table is very useful in identifying and interpreting *KLL* Auger lines, and the interpolated energies are in quite good agreement with new experimental values. However it has now become clear, as more experimental energies of high accuracy have become available, that the theory was incomplete. The necessity to use different forms for the relativistic correction factor in the heavy and light elements constitutes a serious deficiency in the theory. Now that reliable Hartree-Fock values of the two-electron integrals are available from the calculations of Mann,⁸ it is also clear that the values of the two-electron integrals estimated using the larger values of A given by Asaad and Burhop are reasonable, while those estimated using Hörnfeldt's expression are not. For example, the former gives an estimate of $F^0(2s, 2s)_{Zr} = 143.5$ eV, while the latter would give 82.8 eV for this integral. Mann's value is 147.3 eV. Such a large discrepancy is unacceptable: The integral $F^0(2s, 2s)$ is affected very little by environment, etc. Thus the 82.8-eV value cannot be a meaningful estimate of this integral. But Hörnfeldt's value is required if the KL_1L_1 energy is to be fitted by Eqs. (1). We are therefore forced to conclude that a rather large term (~ 70 eV in this case) has been overlooked in the theory. This term is the subject of Sec. III.

III. STATIC RELAXATION ENERGY

Implicit in the derivation of Eqs. (1), as of any similar expression for the Auger energy, is the assumption that the final state can be reached from the initial state through a series of simple steps, each with known energy. The steps for the *KLL'* transition are, for element Z ,

$$Z - Z(\bar{K})^+ + e^- , \quad (3a)$$

$$Z - Z(\bar{L})^+ + e^- , \quad (3b)$$

$$Z(\bar{L})^+ - Z(\bar{L}\bar{L}')^{2+} + e^- . \quad (3c)$$

The energies of the first two processes, $E(3a)$ and $E(3b)$, are indeed known: They are just the binding energies $E(K)$ and $E(L)$. Step (3c) is different, however. Coupling of orbitals \bar{L} and \bar{L}' in the final state can be handled by standard intermediate-coupling methods. This can be done using Eqs. (1), as prescribed by Asaad and Burhop. Let us denote the sum of all the final-state coupling terms in each Auger transition by $\mathcal{F}(X)$, where X labels the transition. Equations (1) can then be written

$$\begin{aligned} E(KL_1L_1; {}^1S) &= E(K) - 2E(L_1) - \mathcal{F}(KL_1L_1; {}^1S), \\ E(KL_2L_3; {}^1D) &= E(K) - E(L_2) - E(L_3) - \mathcal{F}(KL_2L_3; {}^1D), \end{aligned} \quad (4)$$

(and seven other equations),

where the detailed expression for each \mathcal{F} can be obtained by comparison of Eqs. (1) and (4). Use of the Asaad-Burhop equations is thus equivalent to assuming that the binding energy in step (3c) is just the sum $E(L') + \mathcal{F}$; i. e., the one-electron binding energy of the L' orbital in the neutral atom plus the final-state interaction term \mathcal{F} . To test the validity of this assumption let us consider the structure of \mathcal{F} .

If \mathcal{F} were really the difference between $E(L')$ and $E(3c)$, it should account for the differences in binding energies of the L' orbitals in the two initial states; i. e., the neutral atom Z and the ion $Z(\bar{L})^+$. In fact \mathcal{F} accounts only for those differences in the L' binding energy that arise from changes in the L orbital. Thus $F^0(LL')$ is the leading term in \mathcal{F} . We may understand the contribution of $F^0(LL')$ to the sum

$$E(L') + \mathcal{F} = E(L') + F^0(LL') + \dots$$

as representing most of the amount by which the binding energy of the L' orbital is raised from Z to $Z(\bar{L})^+$ because there is a hole in the L orbital in $Z(\bar{L})^+$. This is expected, because $F^0(LL')$ represents most of the electrostatic interaction between electrons in the L' orbital and the L orbital. The remaining terms in \mathcal{F} also describe the effects on the L' binding energy that arise from coupling of the L and L' holes in the final state, including both spin-orbit and electrostatic terms. The formulas given by Asaad and Burhop [of which Eqs. (1) are examples] give a complete description of the coupling of the L and L' hole states. Of course the use of ground-state values⁸ for the LL' two-electron integrals, as well as the ground-state spin-orbit coupling constant, requires the assumption that these quantities do not change appreciably in going from the ground state to the two-hole state. While very small changes in the values of these quantities are expected, appreciable changes are not. Particularly for deep-lying hole states the constraints of the atomic potential are too strong to allow significant variations in these parameters. Empirically, of course, the success of multiplet-structure theory of valence electrons (in which the constraints are much weaker) argues strongly for the constancy of the electrostatic and spin-orbit parameters. The strongest evidence for their constancy will in fact be provided implicitly by the success of our theory (Sec. V). Thus we must look elsewhere to explain the discrepancy between the values of two-electron integrals that are required to fit Eqs. (1) to experiment and values that could be considered reasonable.

Most of the shift in the L' -orbital binding energy can presumably be expressed in terms of changes in two-electron integrals involving L' as one of the orbitals, since the orbital energy $\epsilon(L')$ can be written entirely in terms of one- and two-electron integrals:

$$\epsilon(L') = h(L') + \sum_i [2J(L'i) - K(L'i)]. \quad (5)$$

Here $h(L')$ is the energy of interaction of an electron in the L' orbital with the nucleus, J is a Coulomb integral, and K is an exchange integral. To study changes that a hole in the L orbital would make in the sum over two-electron integrals, we can break this sum into three sums, over "inner"-shell terms—just the K shell in this case—over "intrashell" terms, and over "outer"-shell terms, with principal quantum number $n > 2$.

Hedin and Johansson have considered the problem of passive-orbital relaxation during photoemission.⁹ They calculated the quantity $\langle k | V_p | k \rangle$, defined as the expectation value of a potential due to polarization of the orbitals when an electron in the k orbital is removed. Setting $k = L'$, we have

$$\langle L' | V_p | L' \rangle = \Delta \sum_i [2J(L'i) - K(L'i)], \quad (6)$$

where Δ refers to the difference in the sum with and without the L' orbital occupied, and $\langle L' | V_p | L' \rangle$ is exactly the quantity that we are seeking.

In calculations on sodium and potassium atoms and ions, Hedin and Johansson found that contributions from the inner-shell sum are negligible. The intrashell term is small and apparently fairly constant for these elements [5.55 eV for (Na^+2s), 6.15 eV (Na^+2p), 3.97 eV (K^+2s), and 5.52 eV (K^+2p)]. The outer-shell sum can be large, however. The reason for this is perfectly straightforward. In the neutral atom each L electron shields the electrons in the outer orbitals almost completely from one unit of nuclear charge. When an L vacancy is created the outer orbitals relax inward as if Z had been increased by one unit. This increases the value of all integrals $J(L'i)$ and $K(L'i)$ in the outer-shell sum, because the electrons in outer shells can then interact more strongly with the L' electrons.

The hypothetical two-step path from the neutral atom Z to the doubly ionized species $Z(L'L')^{2+}$ leads to a (somewhat artificial) conceptual separation of the total outer-shell relaxation energy experienced by the L electrons into two parts. We shall call these the dynamic and static relaxation energies. The dynamic terms appear during ionization. The outer orbitals relax adiabatically during the ejection of an L electron, thereby lowering its binding energy. Hedin and Johansson showed that the true binding energy is quite accurately given as the orbital energy plus a dynamic relaxation

term $\frac{1}{2}\langle L | V_p | L \rangle$. Thus for the first ionization step,

$$E(L) = -\epsilon(L) - \frac{1}{2}\langle L | V_p | L \rangle. \quad (7)$$

There is also a dynamic term for the second ionization.

The static relaxation term arises explicitly because of the practice of using the binding energy $E(L')$ of the L' orbital in a neutral atom in Eq. (3c). Denoting by V , V^* , and V^{**} the total two-electron interaction energies of the L or L' orbitals with other orbitals, the two neutral-atom L binding energies in Eqs. (1) can be expanded⁹ as

$$-E(L) - E(L') = h(L) + h(L') + \langle L | V | L \rangle + \frac{1}{2}\langle L | V_p | L \rangle + \langle L' | V | L' \rangle + \frac{1}{2}\langle L' | V_p | L' \rangle, \quad (8)$$

where

$$\langle L | V_p | L \rangle = \langle L | (V^* - V) | L \rangle, \\ \langle L' | V_p | L' \rangle = \langle L' | (V^* - V) | L' \rangle.$$

The correct expression, using the L' binding energy in a unipositive atom $Z(\bar{L})^+$, is

$$-E(3b) - E(3c) \\ = -E(L) - E(L', \text{ in } Z(\bar{L})^+) \\ = h(L) + h(L')^* + \langle L | V | L \rangle + \frac{1}{2}\langle L | V_p | L \rangle \\ + \langle L' | V^* | L' \rangle + \frac{1}{2}\langle L' | V_p^* | L' \rangle, \quad (9)$$

where

$$\langle L' | V_p^* | L' \rangle = \langle L' | (V^{**} - V^*) | L' \rangle.$$

Making approximations at the level made by Hedin and Johansson, omitting the one-electron terms, and shortening the notation to $\langle L | (V^* - V) | L \rangle = V^* - V$, and $\langle L' | (V^* - V) | L' \rangle = V^* - V'$, etc., the remainders of the right-hand sides of Eqs. (8) and (9) become, after substitution,

$$\frac{1}{2}V + \frac{1}{2}V^* + \frac{1}{2}V' + \frac{1}{2}V^{*'} \quad (8')$$

and

$$\frac{1}{2}V + \frac{1}{2}V^* + \frac{1}{2}V^{*'} + \frac{1}{2}V^{**'}. \quad (9')$$

The difference between these two expressions is the static relaxation term, which will be denoted R . Thus

$$R = \frac{1}{2}(V^{**'} - V'). \quad (10)$$

For computational convenience we note that it is a very accurate approximation, at least in the "equivalent-cores" scheme described in what follows, to use

$$R \cong V^{*'} - V', \quad (11)$$

which follows because $V^{**'} - V^{*}'$ is quite accurately equal to $V^{*}' - V'$. The equivalent approximation has been confirmed extensively by direct calculation in the equivalent-cores case.

If we consider the case of two equivalent L electrons, and drop the primes from $V^{*'}$ and $V^{**'}$ in Eq. (9'), the latter expression may be written

$$V + \frac{1}{2}(V^* - V) + V + (V^* - V) + \frac{1}{2}(V^{**} - V^*) . \quad (9'')$$

The first and third terms are initial-state potential energies that are included in the orbital energies ϵ . The second and fifth terms are dynamic relaxation energies, and the fourth is the static relaxation energy. To the very good accuracy with which $2V^* = V + V^{**}$ holds, the total static and dynamic relaxation energies are equal.

The two-step process for reaching the two-hole state is not really necessary. If the two L orbitals are identical, an alternative process can be considered, in which the two electrons come out at the same time. In this process

$$Z - Z(L\bar{L})^{2*} + 2e^- \quad (12)$$

could be treated as one ionization process. By using arguments similar to those of Hedin and Johansson, the energy of this process can be shown to be

$$-E = 2h(L) + 2V + \frac{1}{2}(2V^{**} - 2V) , \quad (13)$$

where the last term is a dynamic relaxation energy. There is formally no static term in this case because the two electrons leave together, but the dynamic term is twice what it was in the two-step process, so that the total relaxation energy is unchanged. To show this we can rewrite the terms in Eq. (13) that are to be compared to those in Eq. (9'):

$$V + V^{**} . \quad (13')$$

If Eq. (9') is applied to a two-step process involving two equivalent electrons the primes on V^* and V^{**} may be dropped. Then, since $2V^*$ is quite accurately equal to $V + V^{**}$, Eqs. (9') and (13') are equivalent, and the Auger energy that would be calculated using the one-step (double) ionization would indeed have the same relaxation energy as in the two-step case.

The matter of dropping the primes above is of some concern. We are constrained in effect to using a two-step approach for actual calculations because we need to use experimental binding energies. The total relaxation energy should not depend on the *order* of the two steps, however. If it did there would be some justification in using an average value for a given transition {i. e., $\frac{1}{2}[R(LL') + R(L'L)]$ }, but it would be preferable for $R(LL')$ and $R(L'L)$ to be at least nearly equal. In fact they are in the calculations in Sec. IV.

To calculate $\langle L' | V_p | L' \rangle$ rigorously we would need L hole-state wave functions for all the elements. However, a rather accurate approximation can be made by substituting the Coulomb and

exchange integrals of the next higher element for the corresponding L hole-state integrals. This "equivalent-cores" approximation has been found to give very good values for $\langle k | V_p | k \rangle$ in estimating atomic binding energies.¹⁰ We shall use this approximation in what follows. We can write as the general expression for the *KLL'* Auger energy associated with the final state X ,

$$E(KLL'; X) = E(K) - E(L) - E(L') - \mathcal{F}(KLL'; X) + R(X). \quad (14)$$

Denoting the intrashell contribution to R by r , neglecting the negligible contribution of inner-shell relaxation, and using the equivalent-cores approximation, we have for the L shell

$$R(2l) = r + \sum_{n'l' \substack{> 2 \\ n'l' > 2}} \frac{N(n'l')}{(4l'+2)} \left[f(l'l') \Delta [F^0(2l, n'l')] - \Delta \sum_k [g_k(l'l') G^k(2l, n'l')] \right]. \quad (15)$$

Here F^0 and G^k are Slater integrals that appear in the expansions of the Coulomb and exchange integrals, respectively. $N(n'l')$ is the population of the $n'l'$ subshell. The coefficients $f(l'l')$ and $g(l'l')$ are readily evaluated using standard multiplet theory.¹¹ They have been given earlier,¹⁰ but are set out in Table I for convenience. These coefficients apply rigorously to closed outer shells, but only relatively small errors are incurred if they are used for open-shell atoms. This amounts to ignoring multiplet coupling between the L electrons and open valence shells.

The Coulomb terms in Eq. (14) all have the form ΔF^0 . The exchange terms can also be written as ΔG^k . The equivalent-cores approximation can be written

$$\begin{aligned} \Delta F^0(2l, n'l') &= F^0(2l, n'l'; Z+1) - F^0(2l, n'l'; Z), \\ \Delta G^k(2l, n'l') &= G^k(2l, n'l'; Z+1) - G^k(2l, n'l'; Z). \end{aligned} \quad (16)$$

Combining Eqs. (13)–(15), we have a strong theoretical basis to predict *KLL* Auger energies.

IV. CALCULATIONS

The calculated Auger energies are given in Table II. Details of the calculation are described in this section.

The binding energies used here were taken from the compilation of Siegbahn *et al.*,⁷ except for the rare gases, for which Ref. 12 was used. Thus, except for the rare gases, the binding energies are referred to the Fermi energy. As Siegbahn *et al.* noted, the precision of these energies is about 1 eV, but uncertainty about the chemical composition of the surface introduces an uncertainty of several eV into many of the binding ener-

TABLE I. The f and g coefficients in Eq. (15).

l	l'	$f(l')$	$g_0(l')$	$g_1(l')$	$g_2(l')$	$g_3(l')$	$g_4(l')$	$g_5(l')$	$g_6(l')$
0	0	2	1						
0	1	6		1					
0	2	10			1				
0	3	14				1			
1	0	2		$\frac{1}{3}$					
1	1	6	1		$\frac{2}{5}$				
1	2	10		$\frac{2}{3}$		$\frac{3}{7}$			
1	3	14			$\frac{3}{5}$		$\frac{4}{9}$		
2	0	2			$\frac{1}{5}$				
2	1	6		$\frac{2}{5}$		$\frac{9}{35}$			
2	2	10	1		$\frac{2}{7}$		$\frac{2}{7}$		
2	3	14		$\frac{3}{5}$		$\frac{4}{15}$		$\frac{10}{33}$	
3	0	2				$\frac{1}{7}$			
3	1	6			$\frac{9}{35}$		$\frac{4}{21}$		
3	2	10		$\frac{3}{7}$		$\frac{4}{21}$		$\frac{10}{77}$	
3	3	14	1		$\frac{4}{15}$		$\frac{2}{11}$		$\frac{100}{429}$

gies.⁷

The $\mathcal{F}(KLL'; X)$ terms were calculated using the Slater integrals of Mann.⁸ Since these are non-relativistic, empirical relativistic correction factors were used. These factors had the form $(1 + aZ^2)$ as prescribed by Asaad,⁶ and the value of a was determined for $F^0(2s, 2s)$, $F^0(2s, 2p)$, and $F^0(2p, 2p)$ by fitting the theory to the experimental Auger energies given in the tabulation of Sevier.¹³ The values 4.2×10^{-5} , 3.5×10^{-5} , and 2×10^{-5} , respectively, were thus determined for the above three integrals. The data were inadequate to determine a values for the $F^2(2p, 2p)$ and $G^1(2s, 2p)$ integrals: Accordingly no relativity corrections were made for these two integrals. It is important to make corrections for the first three integrals, but their accuracy is not critical except for the heavy elements. For $Z = 40, 70,$ and 100 the correction factors for $F^0(2s, 2s)$ (for which the correction itself is largest) are, respectively, 1.07, 1.21, and 1.42. The empirical adjustment of the relativity factors is the weakest feature of this calculation. If Slater integrals from relativistic Hartree-Fock calculations were available, this would not be necessary, and the calculation would have no adjustable parameters whatever. As it is,

uncertainties in the relativity corrections and the corrections themselves are small enough up to $Z = 50$ or 60 that the a factors do not figure as very important parameters in the calculation.

The relaxation energies R were calculated using Eqs. (14) and (15), and employing Mann's Slater integrals. The relaxation terms $R(2s)$ and $R(2p)$ differed by so little (~ 1 or 2 eV) that it was not deemed worthwhile to calculate them separately, and a common value was used (thus the order of the steps in the hypothetical two-stage ionization is really immaterial). The intrashell term r was taken as 6 eV for neon ($Z=10$) and allowed to decrease linearly to zero at argon ($Z=18$) because in this way the total relaxation term R was made to match the polarization energy $\langle 2p | V_p | 2p \rangle$ as given by Hedin and Johansson for Na^+ and K^+ , which are isoelectronic to Ne and Ar. For $Z > 18$ intrashell contributions were neglected. Finally the calculated values of R had to be smoothed somewhat especially through transition series, because the direct use of Eq. (14) is only viable for closed outer shells. The adopted values of R are given in Table II.

The full equations that were used to calculate the Auger energies are

$$E(KL_1L_1) = E(K) + R - 2E(L_1) - F^0(2s, 2s),$$

$$E(KL_1L_2^1P_1) = E(K) + R - E(L_1) - E(L_2) - F^0(2s, 2p) + \frac{3}{4}\xi - \left\{ \left[\frac{1}{3}G^2(2s, 2p) - \frac{1}{4}\xi \right]^2 + \frac{1}{2}\xi^2 \right\}^{1/2},$$

$$\begin{aligned}
E(KL_1L_3^3P_1) &= E(K) + R - E(L_1) - E(L_2) - F^0(2s, 2p) + \frac{3}{4}\zeta + \left\{ \left[\frac{1}{3}G^1(2s, 2p) - \frac{1}{4}\zeta \right]^2 + \frac{1}{2}\zeta^2 \right\}^{1/2}, \\
E(KL_1L_2^3P_0) &= E(K) + R - E(L_1) - E(L_2) - F^0(2s, 2p) + \frac{1}{3}G^1(2s, 2p), \\
E(KL_1L_3^3P_2) &= E(K) + R - E(L_1) - E(L_2) - F^0(2s, 2p) + \frac{1}{3}G^1(2s, 2p) + \frac{3}{2}\zeta, \\
E(KL_2L_3^1D_2) &= E(K) + R - 2E(L_2) - F^0(2p, 2p) + \frac{2}{25}F^2(2p, 2p) + \frac{3}{4}\zeta - \left\{ \left[\frac{3}{25}F^2(2p, 2p) + \frac{1}{4}\zeta \right]^2 + \frac{1}{2}\zeta^2 \right\}^{1/2}, \\
E(KL_3L_3^3P_2) &= E(K) + R - 2E(L_2) - F^0(2p, 2p) + \frac{2}{25}F^2(2p, 2p) + \frac{3}{4}\zeta + \left\{ \left[\frac{3}{25}F^2(2p, 2p) + \frac{1}{4}\zeta \right]^2 + \frac{1}{2}\zeta^2 \right\}^{1/2}, \\
E(KL_3L_3^3P_0) &= E(K) + R - 2E(L_2) - F^0(2p, 2p) - \frac{1}{10}F^2(2p, 2p) + \frac{3}{2}\zeta + \left\{ \left[\frac{3}{10}F^2(2p, 2p) - \frac{1}{2}\zeta \right]^2 + 2\zeta^2 \right\}^{1/2}, \\
E(KL_2L_2^1S_0) &= E(K) + R - 2E(L_2) - F^0(2p, 2p) - \frac{1}{10}F^2(2p, 2p) + \frac{3}{2}\zeta - \left\{ \left[\frac{3}{10}F^2(2p, 2p) - \frac{1}{2}\zeta \right]^2 + 2\zeta^2 \right\}^{1/2}. \quad (17)
\end{aligned}$$

V. DISCUSSION

The values in Table II represent the only comprehensive set of theoretical *KLL* Auger energies. They should provide the best estimates of *KLL* energies in all cases for which neither accurate experimental values nor two-hole-state Hartree-Fock (or Dirac-Fock) calculations are available. They show excellent agreement with experiment, as discussed in this section. The KL_1L_1 energies, which were reported earlier,¹ are treated separately first because they are independent of intermediate coupling in the final state.

Table III lists the KL_1L_1 energies from this work, the semiempirical values,⁷ and experimental values, for elements in which experimental values are available.¹³ The experimental values have a wide range of accuracy and reliability. In some elements, several experimental values were available. For these cases either an average was taken or a single value chosen, depending on the relative accuracy of the results. The agreement between experiment and theory is excellent. For neon, the single rare gas in Table III, the accuracy of the binding energies is such that the 3-eV difference probably signifies that the 6-eV intrashell relaxation energy is an overestimate. The estimate of 751 eV is, however, much closer to experiment than the semiempirical value of 761 eV. The other thirty-eight cases in Table III were studied experimentally as solids, and questions of the surface oxidation state probably introduce an uncertainty of ~ 5 eV into the comparison of theory and experiment. With this uncertainty added, 31 of the 38 estimates fall within the ranges of experimental uncertainty. In 23 of the 39 cases Eqs. (17) predict the experimental values more accurately even than do the semiempirical energies (two cases are even, and the semiempirical energies are closer in 14 cases). We conclude that Eq. (17) is quite accurately valid for predicting KL_1L_1 energies, which involve the relaxation term and the single Slater integral $F^0(2s, 2s)$ in addition to empirical binding energies.

To test the accuracy of using the other tabulated Slater integrals in the intermediate coupling calcu-

lation, as well as the relaxation-energy calculation for lines involving $2p$ electrons, let us compare the other eight predicted *KLL* energies with experiment. Although experimental *KLL* Auger energies are available for forty-four of the 91 elements for which theoretical values are listed in Table II, the wide variation in accuracy and completeness of these data renders exhaustive comparison of all the data unnecessary. Therefore, for brevity, the data on only nine elements were selected for comparison with theory. These elements, $Z=10, 19, 29, 40, 53, 62, 71, 83,$ and 94 , were chosen (a) to give representative coverage of the Periodic Table, (b) to use the more accurate and complete data available subject to (a),

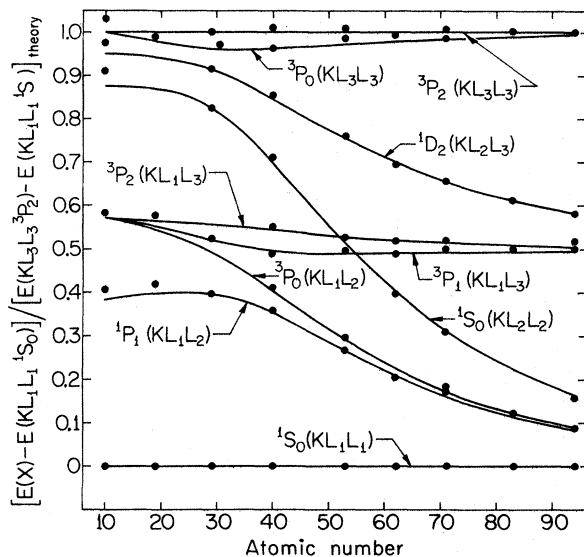


FIG. 1. Reduced *KLL* Auger-energy differences for the elements. Here $E(X)$ is the experimental energy of component X . The nine components are labeled on the plot. In the ordinate ratio the denominator is always the total theoretical spacing, from Table II. The curves are theoretical, obtained by using theoretical energies from Table II in the numerator. Filled circles were obtained by using experimental values from Ref. 13 in the numerator. Thus there is no scaling to fit experiment to theory.

TABLE II. Predicted *KLL* Auger energies (eV).

El.	<i>Z</i>	<i>R</i>	¹ <i>S</i> ₀ <i>KL₁L₁</i>	¹ <i>P</i> ₁ <i>KL₁L₂</i>	³ <i>P</i> ₁ <i>KL₁L₃</i>	³ <i>P</i> ₀ <i>KL₁L₂</i>	³ <i>P</i> ₂ <i>KL₁L₃</i>	¹ <i>D</i> ₂ <i>KL₂L₃</i>	³ <i>P</i> ₂ <i>KL₃L₃</i>	³ <i>P</i> ₀ <i>KL₃L₃</i>	¹ <i>S</i> ₀ <i>KL₂L₂</i>
Ne	10	6	751	774	785	785	785	806	809	809	802
Na	11	8	922	948	961	961	961	986	989	989	981
Mg	12	10	1 101	1 131	1 145	1 145	1 145	1 174	1 178	1 178	1 168
Al	13	12	1 296	1 332	1 348	1 348	1 348	1 383	1 388	1 387	1 376
Si	14	14	1 511	1 550	1 568	1 568	1 569	1 607	1 612	1 611	1 599
P	15	16	1 739	1 781	1 800	1 800	1 801	1 841	1 848	1 847	1 833
S	16	18	1 980	2 032	2 053	2 052	2 053	2 103	2 110	2 109	2 094
Cl	17	20	2 247	2 302	2 325	2 324	2 326	2 379	2 386	2 384	2 368
Ar	18	22	2 524	2 584	2 608	2 607	2 609	2 666	2 674	2 672	2 654
K	19	25	2 814	2 880	2 906	2 905	2 908	2 970	2 979	2 976	2 957
Ca	20	28	3 121	3 194	3 221	3 220	3 223	3 292	3 302	3 299	3 279
Sc	21	31	3 451	3 529	3 557	3 555	3 560	3 633	3 645	3 640	3 619
Ti	22	33	3 793	3 880	3 910	3 907	3 913	3 995	4 008	4 003	3 980
V	23	36	4 163	4 256	4 286	4 283	4 290	4 376	4 390	4 384	4 360
Cr	24	39	4 552	4 647	4 679	4 676	4 685	4 772	4 789	4 781	4 754
Mn	25	42	4 953	5 054	5 088	5 083	5 094	5 187	5 205	5 196	5 167
Fe	26	45	5 373	5 480	5 515	5 509	5 522	5 620	5 640	5 631	5 598
Co	27	48	5 806	5 922	5 959	5 953	5 968	6 073	6 095	6 085	6 049
Ni	28	51	6 265	6 385	6 423	6 416	6 433	6 541	6 566	6 554	6 516
Cu	29	54	6 734	6 863	6 903	6 894	6 914	7 030	7 058	7 045	7 002
Zn	30	57	7 216	7 351	7 393	7 382	7 405	7 525	7 556	7 542	7 495
Ga	31	58	7 713	7 744	7 873	7 884	7 778	7 802	7 904	8 009	7 782
Ge	32	60	8 218	8 367	8 414	8 398	8 430	8 562	8 602	8 586	8 524
As	33	61	8 749	8 903	8 953	8 934	8 970	9 105	9 149	9 132	9 063
Se	34	62	9 283	9 447	9 500	9 478	9 518	9 662	9 710	9 693	9 616
Br	35	63	9 839	10 012	10 069	10 043	10 089	10 241	10 295	10 276	10 188
Kr	36	65	10 411	10 592	10 653	10 623	10 675	10 834	10 894	10 874	10 775
Rb	37	67	10 994	11 184	11 249	11 214	11 273	11 437	11 505	11 484	11 372
Sr	38	68	11 593	11 792	11 863	11 822	11 889	12 060	12 136	12 114	11 987
Y	39	70	12 211	12 419	12 497	12 449	12 524	12 703	12 787	12 764	12 622
Zr	40	72	12 849	13 065	13 150	13 095	13 179	13 364	13 457	13 433	13 274
Nb	41	73	13 501	13 725	13 819	13 756	13 850	14 042	14 145	14 120	13 942
Mo	42	75	14 176	14 409	14 512	14 439	14 544	14 744	14 858	14 832	14 633
Tc	43	76	14 862	15 105	15 217	15 135	15 251	15 459	15 583	15 557	15 337
Ru	44	78	15 570	15 820	15 944	15 851	15 980	16 194	16 331	16 304	16 059
Rh	45	80	16 294	16 554	16 689	16 584	16 726	16 948	17 099	17 071	16 801
Pd	46	81	17 034	17 303	17 452	17 333	7 491	17 720	17 887	17 858	17 556
Ag	47	83	17 793	18 070	18 233	18 100	18 273	18 510	18 692	18 662	18 331
Cd	48	85	18 563	18 849	19 028	18 880	19 069	19 313	19 512	19 481	19 119
In	49	85	19 347	19 642	19 839	19 673	19 881	20 134	20 351	20 320	19 920
Sn	50	86	20 149	20 454	20 668	20 485	20 712	20 973	21 209	21 177	20 740
Sb	51	87	20 968	21 282	21 517	21 313	21 562	21 831	22 090	22 057	21 576
Te	52	88	21 806	22 130	22 386	22 161	22 432	22 710	22 991	22 957	22 433
I	53	88	22 659	22 992	23 271	23 024	23 319	23 604	23 909	23 874	23 303
Xe	54	89	23 516	23 862	24 166	23 894	24 216	24 514	24 846	24 810	24 186
Cs	55	90	24 415	24 766	25 095	24 798	25 146	25 447	25 805	25 769	25 093
Ba	56	92	25 320	25 680	26 038	25 713	26 090	26 400	26 788	26 751	26 018
La	57	93	26 239	26 613	27 001	26 646	27 054	27 377	27 795	27 758	26 963
Ce	58	95	27 190	27 573	27 993	27 606	28 047	28 377	28 829	28 790	27 930
Pr	59	96	28 161	28 553	29 007	28 587	29 063	29 402	29 889	29 850	28 920
Nd	60	98	29 153	29 556	30 047	29 590	30 104	30 453	30 978	30 937	29 933
Pm	61	99	30 160	30 574	31 104	30 609	31 162	31 521	32 085	32 044	30 962
Sm	62	101	31 188	31 613	32 183	31 648	32 243	32 611	33 217	33 175	32 010
Eu	63	103	32 238	32 762	33 288	32 707	33 348	33 725	34 378	34 335	33 078
Gd	64	104	33 305	33 750	34 412	33 786	34 474	34 861	35 561	35 517	34 167
Tb	65	105	34 393	34 850	35 560	34 886	35 623	36 020	36 769	36 725	35 277
Dy	66	107	35 503	35 970	36 733	36 006	36 797	37 204	38 007	37 962	36 407

TABLE II. (Continued)

El.	Z	R	1S_0 KL_1L_1	1P_1 KL_1L_2	3P_1 KL_1L_3	3P_0 KL_1L_2	3P_2 KL_1L_3	1D_2 KL_2L_3	3P_2 KL_3L_3	3P_0 KL_3L_3	1S_0 KL_2L_2
Ho	67	109	36 633	37 110	37 929	37 147	37 995	38 411	39 271	39 226	37 557
Er	68	110	37 781	38 270	39 148	38 307	39 214	39 641	40 561	40 514	38 728
Tm	69	112	38 953	39 453	40 393	39 490	40 460	40 898	41 881	41 833	39 921
Yb	70	113	40 146	40 657	41 662	40 696	41 731	42 180	43 227	43 180	41 138
Lu	71	115	41 359	41 882	42 956	41 921	43 026	43 486	44 604	44 555	42 374
Hf	72	117	42 588	43 123	44 269	43 162	44 340	44 811	46 003	45 953	43 627
Ta	73	118	43 832	44 379	45 601	44 418	45 673	46 155	47 423	47 373	44 893
W	74	120	45 097	45 657	46 961	45 697	47 034	47 529	48 879	48 828	46 185
Re	75	121	46 387	46 961	48 349	47 001	48 423	48 930	50 366	50 314	47 501
Os	76	122	47 694	48 280	49 760	48 321	49 835	50 355	51 883	51 830	48 834
Ir	77	123	49 026	49 625	51 198	49 666	51 275	51 807	53 430	53 376	50 190
Pt	78	124	50 382	50 993	52 666	51 035	52 744	53 287	55 010	54 956	51 571
Au	79	126	51 761	52 385	54 163	52 427	54 242	54 799	56 628	56 573	52 976
Hg	80	127	53 160	53 795	55 683	53 838	55 763	56 329	58 269	58 213	54 397
Tl	81	129	54 567	55 221	57 224	55 264	57 305	57 890	59 946	59 889	55 842
Pb	82	130	56 007	56 673	58 800	56 717	58 882	59 479	61 659	61 601	57 306
Bi	83	132	57 468	58 153	60 405	58 197	60 488	61 103	63 409	63 351	58 804
Po	84	133	58 939	59 640	62 030	59 685	62 115	62 745	65 190	65 131	60 307
At	85	135	60 450	61 165	63 695	61 210	63 781	64 424	67 011	66 951	61 846
Ru	86	136	62 006	62 725	65 401	62 770	65 488	66 136	68 869	68 809	63 410
Fr	87	137	63 552	64 292	67 125	64 338	67 213	67 882	70 772	70 711	64 999
Ra	88	138	65 134	65 895	68 892	65 941	68 981	69 670	72 726	72 664	66 622
Ac	89	139	66 754	67 519	70 688	67 566	70 778	71 471	74 699	74 636	68 250
Th	90	140	68 379	69 167	72 516	69 214	72 607	73 322	76 731	76 667	69 920
Pa	91	141	70 056	70 856	74 393	70 904	74 485	75 212	78 809	78 745	71 622
U	92	142	71 748	72 567	76 302	72 615	76 395	77 141	80 938	80 873	73 353
Np	93	143	73 486	74 317	78 703	74 366	78 797	79 554	84 002	83 936	75 115
Pu	94	144	75 257	76 103	80 266	76 153	80 362	81 134	85 360	85 293	76 916
Am	95	145	77 116	77 956	82 349	78 006	82 446	83 211	87 669	87 601	78 763
Cm	96	146	78 928	79 620	84 422	79 670	84 519	85 137	90 003	89 935	80 279
Bk	97	147	80 660	81 562	86 447	81 613	86 546	87 373	92 323	92 254	82 431
Cf	98	148	83 352	84 224	89 496	84 276	89 596	90 393	95 731	95 661	85 064
Es	99	149	85 294	86 187	91 748	86 239	91 849	92 666	98 294	98 224	87 047
Fm	100	150	87 286	88 190	94 050	88 242	94 152	94 980	100 908	100 837	89 061

and (c) to favor the more chemically stable elements, subject to (a) and (b).

The comparison is made in Fig. 1, which is a "reduced" intermediate-coupling plot of the quantity.

$$\frac{E(X) - E(KL_1L_1)}{[E(KL_3L_3\ ^3P_2) - E(KL_1L_1\ ^1S_0)]_{\text{theory}}}$$

versus Z . The curves in Fig. 1 were drawn by connecting points obtained by using the theoretical energies in Table II in both the numerator and denominator above. The points in Fig. 1 were obtained by inserting experimental energies from Ref. 13 into the numerator, while retaining the theoretical denominator. Thus the ordinate scale in Fig. 1 is *not adjusted between theory and experiment*. This constitutes an extremely stringent test of the theory embodied in Eqs. (17).

From the excellent agreement we conclude:

(i) It is quite accurately valid to use the same

values of R for $2s$ and $2p$ electrons generally. The small positive deviations of the experimental points involving $2p$ electrons in the lightest elements provide some basis for believing that $R(2p)$ is slightly larger than $R(2s)$ for these cases. The ordinate in Fig. 1 is designed to display differences in $R(2s)$ and $R(2p)$ as a systematic deviation of all points, save those for the $KL_1L_1\ ^1S_0$ lines, from their curves.

(ii) The spin-orbit coupling constant ζ for a two-hole state in the L shell is accurately equal to that of a one-hole state. This follows because ζ was calculated in each case from the L_2 and L_3 binding energies.

(iii) The Slater integrals calculated by Mann,⁸ together with Eqs. (17), give a very accurate description of multiplet structure in the two-hole states.

The plot shown in Fig. 1 was suggested by those that Siegbahn *et al.*⁷ and Sevier¹³ have given. The

TABLE III. Comparison of KL_1L_1 energies (in eV).

Z	E_{th}^a	E_{expt}^b	E_{SE}^c	Z	E_{th}^a	E_{expt}^b	E_{SE}^c
10	751	748.0(4)	761	56	25 320	25 251(6)	25 330
11	922	922.8(4)	928	62	31 188	31 175(20)	31 199
12	1 101	1 101.3(4)	1 105	63	32 238	32 224(20)	32 247
19	2 814	2 809	2 815	65	34 393	34 430(50)	34 402
23	4 163	4 159(6)	4 168	66	35 502	35 496(6)	35 512
25	4 953	4 962(2)	4 956	69	38 953	38 958(25)	38 958
26	5 373	5 376	5 374	70	40 146	40 149(4)	40 151
29	6 734	6 735(6)	6 732	71	41 359	41 351(10)	41 361
30	7 216	7 220(4)	7 214	74	45 097	45 080(40)	45 097
32	8 218	8 212(6)	8 216	75	46 387	46 400(25)	46 385
33	8 749	8 742(10)	8 749	78	50 382	50 370(100)	50 375
35	9 839	9 860(10)	9 840	79	51 761	51 780(20)	51 752
38	11 593	11 584.4(16)	11 595	80	53 160	53 141(25)	53 149
40	12 849	12 851.8(15)	12 851	81	54 567	54 510(100)	54 554
42	14 176	14 176.1(13)	14 179	83	57 468	57 467(30)	57 451
47	17 793	17 740(60)	17 797	84	58 939	58 920(50)	58 918
49	19 347	19 352(1)	19 354	92	71 748	71 738(20)	71 704
52	21 806	21 787(10)	21 814	93	73 486	73 555(150)	73 437
53	22 659	22 652(10)	22 668	94	75 257	75 180(15)	75 204
55	24 415	24 395(14)	24 426				

^aThis work.^bFrom Ref. 13. Errors in last place given parenthetically. Some values are selected or averages.^cSemiempirical values from Ref. 7.

nature of the ordinate scales is very different, however: No adjustment has been made in Fig. 1, which therefore really constitutes an "unnormalized" comparison of theory and experiment.

Extension of this approach to other problems should be feasible. For other Auger spectra in which the final state involves two holes in inner shells, this theory is applicable as it stands. Final states with outer-shell vacancies will require different estimates of R . Of course the relaxation-energy concept can be usefully applied to any problem involving multiple-hole final states, not only to Auger spectra.

At this point the KLL Auger energies of the elements can, in all cases except rare gases, be

estimated by Eq. (17) to sufficient accuracy that the remaining small differences between theory and experiment could be largely attributed to uncertainties involving chemical shifts in the surfaces of the thin samples used to determine the binding energies and/or Auger energies. As measurements on well-characterized surfaces become available, it should be possible to detect chemical and solid-state shifts in Auger energies, as well as to test the relaxation theory more quantitatively.

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