Simple model for K x-ray and Auger-electron energy shifts in heavy-ion collisions*

D. Burch and L. Wilets
Department of Physics, University of Washington, Seattle, Washington 98195

W. E. Meyerhof
Department of Physics, Stanford University, Stanford, California 94305
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K x-ray and Auger-electron energies in heavy-ion collisions are shifted in energy in an opposite manner as the degree of ionization in the L shell increases. X-rays are shifted to higher energies and Auger electrons to lower energies. We describe a very simple model which accounts for these effects and provide crude estimates of the shifts.

If x-rays or Auger electrons are produced in heavy-ion collisions, their energies are shifted in an opposite manner with respect to the normal (diagram) energies obtained by electron or proton excitation. Shifts in K-shell transitions have been traced to varying degrees of multiple L-shell ionization which are created in the heavy-ion collision simultaneously with the K vacancy. Missing M and higher-shell electrons have only a small effect on the K-shell transition energies. In the case of x-ray measurements, the shifts have been determined with high enough precision to resolve the shift due to each additional vacancy separately.[1-3] In Auger-electron measurements, structure has been observed corresponding to one and two vacancies,[4] but the spectra are much more complicated than the corresponding x-ray spectra. When higher degrees of multiple ionization are present, individual electron lines usually cannot be resolved.[5] An exception to this is the case when the degree of ionization is so large that the number of remaining transitions is small. Dahl *et al.*[6] have observed sharp L-shell transitions of the type $1s^2 2s^2 2p^5 3s^2 \rightarrow 1s^2 2s^2 2p^6$ emitted from S^{5+} projectiles following low-energy collisions with Ar. In this case the degree of multiple ionization present ($3p^{-4}$) is the maximum consistent with an Auger transition. Corresponding K-shell transitions might be present in higher-energy collisions but have not been reported so far.

Early observations of x-ray energy shifts[7] were interpreted on the basis of Hartree-Fock-Slater (HFS) calculations. Larkins[8] has reported more accurate Hartree-Fock (HF) calculations of Ne and Ar x-ray and Auger transition energies as a function of the degree of outer-shell ionization. Similar calculations have been carried out by Bhalla *et al.*[9] In multiply ionized configurations the x-ray energies increase with increasing degree of ionization, but the Auger electron energies decrease. Published computer codes are available[10] for calculating these transition energies with the accuracy necessary for the interpretation of spectral measurements. The purpose of the present note is to describe a simple atomic model which gives some intuitive feeling for the magnitude and direction of the effects and can be used for estimates.

Figure 1 shows a schematic level diagram of the electron shells of interest with and without a permanent $2p$ vacancy. "Permanent" means here that this vacancy has a lifetime which is longer than that of a K vacancy. For atoms with atomic numbers greater than ~20 this usually requires that the M shell is also sufficiently ionized to reduce the L-MM Auger transition rates. Otherwise the L vacancy would be filled before the K vacancy and the K-shell transition energies would be shifted less.[2]

As illustrated in Fig. 1, removal of the $2p$ electron increases the binding energy of each of the levels. The unshifted and shifted $K\alpha$ x-ray energies are indicated, making no distinction between $K\alpha_1$ and $K\alpha_2$. We use the sudden approximation in which the transition energies are defined as differences in binding energies. The transition energy shifts are then given for x-rays by

$$\Delta K\alpha = \Delta K - \Delta L, \tag{1}$$

$$\Delta K\beta = \Delta K - \Delta M, \tag{2}$$

and for Auger electrons by

$$\Delta K_{LL} = \Delta K - 2\Delta L, \tag{3}$$

$$\Delta K_{LM} = \Delta K - \Delta L - \Delta M, \tag{4}$$

where ΔK, ΔL, and ΔM are the shifts in the binding energies. From Eqs. (1) and (3) we see that the opposite shifts of $K\alpha$ and K-LL require that

$$\Delta L < \Delta K < 2\Delta L. \tag{5}$$

In the following we show that Eq. (5) is a consequence of the change in electrostatic potential which results from the removal of a $2p$ electron.

In the simplest model, the charge of the $2p$ electrons can be considered concentrated in a spherical shell of radius $a_L = 4a_0/Z_L$, where a_0 is the Bohr radius and $Z_L = Z - 4.15$ is the effective charge at the L shell determined from the Slater screening rules.[11] Inside the shell the potential has a constant value of $e^2/a_L = Z_L/4$ a.u. (1 a.u. $= e^2/a_0 = 27.2$ eV); outside it falls off as $1/r$. This is illustrated in Fig. 2 with a dashed line. (The radial electron distributions of the shells of interest are shown to clarify the scale.)

Although this simplest model is not adequate for the present considerations, it is straightforward to calculate the potential more accurately from the expression (in a.u.)

$$V_{2p}(r) = \frac{1}{r} - \frac{4\pi}{r}\int_r^\infty \rho_{2p}(r')(r'^2 - rr')\,dr' , \qquad (6)$$

where, using hydrogenic wave functions,

$$\rho_{2p}(r) = \psi_{2p}^2(r) \propto r^2 e^{-Z_L r} . \qquad (7)$$

Equation (6) is easily verified by checking that $\nabla^2 V = -4\pi\rho$. After integration and normalization,

$$V_{2p}(x) = (Z_L/x)[1 - \tfrac{1}{24}e^{-x}(x^3 + 6x^2 + 18x + 24)], \quad (8)$$

where $x = Z_L r/a_0$. This potential is shown in Fig. 2 with the solid line. Although it is quite similar to the charged-shell result, the difference is significant in the region of the L shell which has a large effect on the energy shifts. The binding energy shifts are given by

$$\begin{aligned} \Delta K &= \langle 1s\,|\,V_{2p}\,|\,1s\rangle = F(Z_K/Z_L)Z_L \simeq 0.243 Z_L , \\ \Delta L &= \langle 2p\,|\,V_{2p}\,|\,2p\rangle = 93/2^9 Z_L \simeq 0.182 Z_L , \\ \Delta M &= \langle 3p\,|\,V_{2p}\,|\,3p\rangle = G(Z_M/Z_L)Z_L \simeq 0.082 Z_L , \end{aligned} \qquad (9)$$

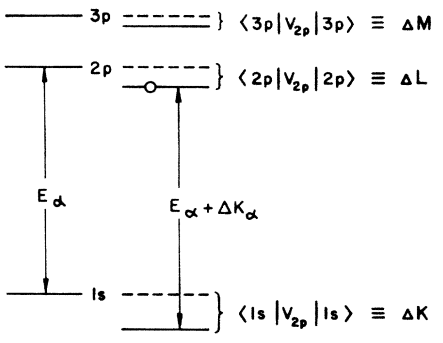

FIG. 1. Binding-energy level diagram for the removal of a $2p$ electron. The binding energy of each level is increased.

where the integrations have been carried out analytically using hydrogenic wave functions[11] with $Z_K = Z - 0.3$ and $Z_M = Z - 11.25$. F and G are slowly varying polynomials in the indicated variables; F varies from 0.248 to 0.243 for $Z = 10$ to 80, and G varies from 0.072 at $Z = 20$ to 0.087 at $Z = 80$. The use of a mean value for G results in a maximum numerical error in the energy shifts of 6%. These values satisfy condition (5) and hence will reproduce opposite shifts for $K\alpha$ and K-LL energies with $2p$ electron removal.

From Eqs. (1)–(4), the energy shifts per $2p$ vacancy are given (in eV) for x-rays by

$$\Delta K\alpha = +1.66 Z_L , \quad \Delta K\beta = +4.38 Z_L ,$$

and for Auger electrons by (10)

$$\Delta K_{LL} = -3.29 Z_L , \quad \Delta K_{LM} = -0.57 Z_L ,$$

where $Z_L = Z - 4.15$. It is seen that the K-LL Auger shift is twice as large and the $K\beta$ x-ray shift and 2.6 times as large as the $K\alpha$ shift. The K-LM Auger energies are the least affected by a $2p$ vacancy. At intermediate and high Z, we know from HFS calculations[12] that x-ray shifts due to a $2p$ vacancy are nearly identical to those of a $2s$ vacancy. Hence, within the present accuracy, Eqs. (10) can be considered valid for any L vacancy.

A comparison of the x-ray shifts [Eqs. (10)] with the HFS calculations of Wolter[12] is shown in Fig. 3. The model values are surprisingly accurate at high Z. At low Z the agreement is worse; at $Z = 20$ the disagreement is ~20%. Recent measurements of Kauffman *et al.*,[3] however, show that even in Ne the shift due to five vacancies corresponds to 9.4 eV per vacancy, which agrees

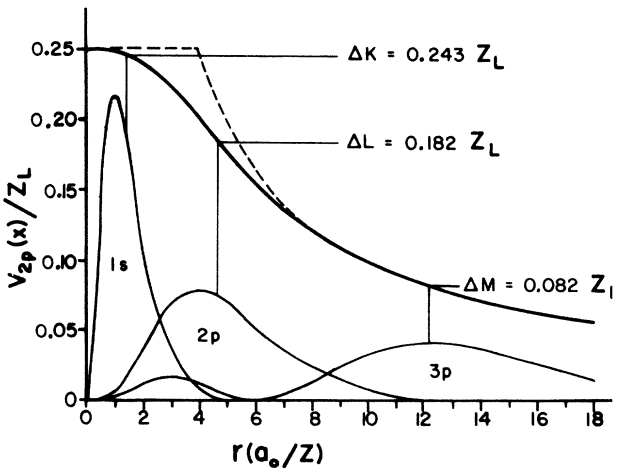

FIG. 2. Electrostatic potential due to a $2p$ electron calculated for a charged-shell (dashed curve) and hydrogenic charge distribution (solid curve). Radial electron distributions are also shown.

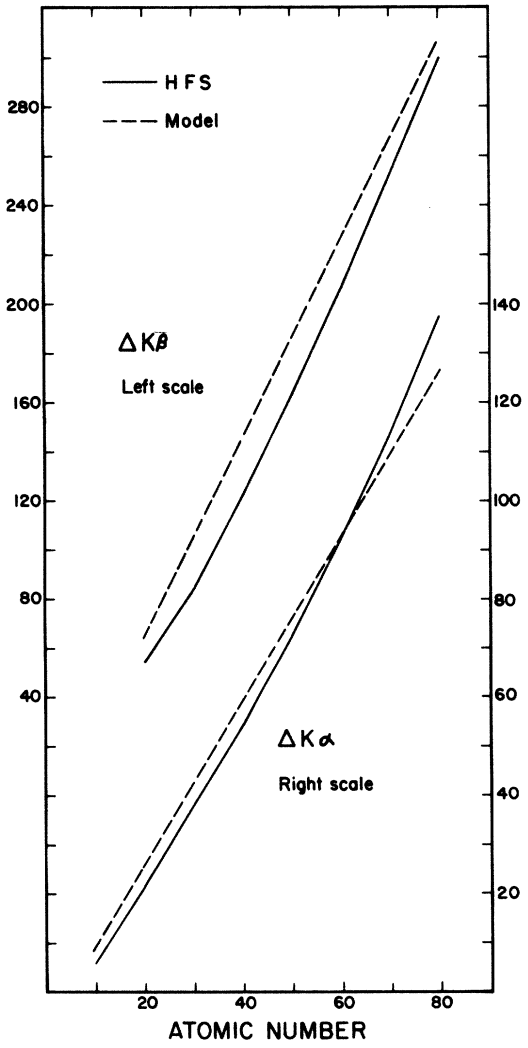

FIG. 3. K x-ray energy shifts in eV due to a missing $2p$ electron. The HFS results of Ref. 12 (solid curves) are compared to the simple model discussed in the text (dashed curves).

favorably with the model prediction of 9.7 eV. (For higher Z the x-ray shift per vacancy is nearly independent of the number of vacancies.)

For the Auger shift in Ne, full HF calculations

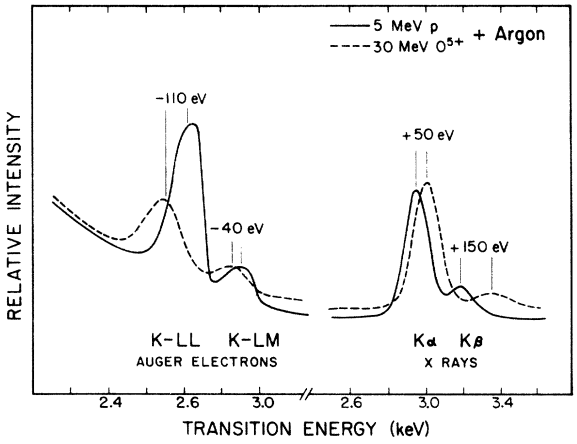

FIG. 4. K x-ray and Auger electron spectra of Ar produced by 30-MeV oxygen ions (dashed curves) and 5-MeV protons (solid curves). The indicated energy shifts are due to multiple ionization as discussed in the text.

yield[8] $\Delta K_{LL} = 19.3$ eV and the model predicts 19.2 eV. This good agreement, which may be accidental, is valid only for $Z \lesssim 30$. At higher Z, HFS calculations show that the magnitude of ΔK_{LL} approaches that of $\Delta K\alpha$, contrary to Eqs. (10).

Figure 4 illustrates how these effects appear experimentally in low resolution. The data are from the University of Washington using a Si(Li) detector for the x rays and a cylindrical-mirror analyzer at 90° for the electrons. Using Eqs. (10) to see whether a consistent average number of L vacancies can be predicted from the centroid shifts, we find from $\Delta K\alpha$, $\Delta K\beta$, ΔK_{LL}, and ΔK_{LM}, respectively, 2.2, 2.5, 2.4, and 5.0. The inconsistency of ΔK_{LM} is not surprising, since the outer-shell Auger rates are strongly affected by M vacancies—an effect which can distort the centroid energy.[5]

In conclusion, we have shown that a simple model can be made to account for the effects of L-shell ionization on K-shell transition energies. The model can easily be extended to arbitrary defect configurations and to L-shell transitions.

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[1]A. R. Knudson, D. J. Nagel, P. G. Burkhalter, and K. L. Dunning, Phys. Rev. Lett. 26, 1149 (1971).

[2]D. Burch, P. Richard, and R. L. Blake, Phys. Rev. Lett. 26, 1355 (1971).

[3]R. L. Kauffman, F. Hopkins, C. W. Woods, and P. Richard, Phys. Rev. Lett. 31, 621 (1973).

[4]N. Stolterfoht, in *Inner Shell Ionization and Future Applications*, edited by R. W. Fink *et al.* (U. S. AEC, Oak Ridge, Tenn., 1973), p. 1043; N. Stolterfoht, F. J. de Heer, and J. Van Eck, Phys. Rev. Lett. 30, 1159 (1973).

[5]D. Burch, W. B. Ingalls, J. S. Risley, and R. Heffner, Phys. Rev. Lett. 29, 1719 (1973); D. Burch, W. B. Ingalls, H. Wieman, and J. S. Risley (unpublished).

[6]P. Dahl, B. Fastrup, G. Hermann, M. E. Rudd, and M. Rødbro, *VIII ICPEAC Abstracts*, edited by B. C. Čobić and M. V. Kurepa (Institute of Physics, Belgrade, 1973), p. 708.
[7]D. Burch and P. Richard, Phys. Rev. Lett. 25, 983 (1971).
[8]F. P. Larkins, J. Phys. B 4, 1 (1971); J. Phys. B 4, 14 (1971).
[9]C. P. Bhalla, N. O. Folland, and M. Hein, Phys. Rev. A 8, 649 (1973).
[10]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, N. J., 1963); for greater accuracy see C. Frose Fischer, Computer Phys. Commun. 4, 107 (1972).
[11]J. C. Slater, Phys. Rev. 36, 57 (1930).
[12]H. Wolter (private communication); D. Burch, H. Wolter, and P. Richard (unpublished).