

Multiple Electron Excitation in Auger Processes*

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(Received April 18, 1955)

Consideration of the Auger effect as a polyelectron phenomenon leads to the expectation of an accumulation of a greater charge on an atom, as the result of an Auger cascade, than that obtainable by the conventional two-electron theory. On this basis, calculations are made of the probability for the accumulation of large charges by chlorine atoms originally possessing a K vacancy. The theoretical results correlate well with the recent experimental measurements of the charge distribution of the chlorine atoms produced by the electron-capture decay of argon-37.

THE Auger process is usually described as a process involving two bound atomic electrons, one of which undergoes a transition to a vacant orbital of lower energy while the other one is ejected to the continuum. The charge on the atom is thus increased by one unit.

In the nonrelativistic theory of the Auger effect, the probability of a transition between two atomic states of the same energy ψ_i and ψ_f is proportional to M ,¹ where

$$M = \left| \int \psi_f^* \sum_{s>j} \frac{e^2}{r_{sj}} \psi_i d\tau \right|^2. \quad (1)$$

In the evaluation of M , ψ_f and ψ_i are usually taken to be properly antisymmetrized two-electron atomic orbital wave functions for the two electrons involved in the process; the other electrons in the polyelectronic atom are ignored. In the atomic orbital approximation, this procedure is justified if the assumption is made that the orbitals of the other electrons are the same in both ψ_f and ψ_i and thus have orthogonality properties such that e^2/r_{sj} can connect only states which differ in the orbitals of two electrons.

Since one generally finds that the orbitals of the other electrons also must change due to a change in screening constants, the above description of the process as a two-electron problem is not quite complete. Those bound electrons which have velocities small compared to that of the ejected "Auger" electron suffer a "sudden perturbation" due to the sudden change in effective nuclear charge and may undergo a transition to an excited state. This situation is similar to the case of the sudden perturbation in beta decay, which has been studied by a number of investigators.² Thus for these electrons, the wave function ψ_f in Eq. (1) should be written with effective values of the nuclear charge computed with allowance for the missing Auger electron. There exists then a probability that an atom may gain

more than one charge as a result of an Auger process, if one of the other electrons is excited either to a continuum state or to a bound state capable of participating later in an Auger process which would otherwise not have been possible.

Computations of the above effect have been made for Auger transitions in chlorine, which are of special interest on account of recent experimental measurements of the average charge³ and also of the actual charge distribution⁴ of chlorine atoms resulting from the electron capture decay of argon-37. The effective Z values for the various atomic orbitals were found using the Slater recipes.⁵ From the values of ΔZ and with the aid of tabulations made by Schwartz,² one sees immediately that only certain Auger transitions will give rise to a significant amount of multiple excitation. These cases include $3s$ and $3p$ excitation accompanying the Auger transition $K \rightarrow LL$;⁶ $3s$ and $3p$ excitation accompanying $L_I \rightarrow L_{II, III}M$; $2s$, $2p$, $3s$, and $3p$ excitation accompanying $L \rightarrow MM$. Of these, however, $3s$ and $3p$ excitation accompanying $L_I \rightarrow L_{II, III}M$ and $2s$ and $2p$ excitation accompanying $L \rightarrow MM$ are both energetically impossible. The other two above Auger processes which may be accompanied by $3s$ and $3p$ excitation fulfill not only the energy requirements but also the requirements which make the sudden perturbation treatment applicable. By means of the Auger phenomenon alone chlorine of charge plus 5 can be produced following the K -capture decay of argon by the following set of five processes: $K \rightarrow L_I L_I$, $L_I \rightarrow L_{II, III}M$, $L_I \rightarrow L_{II, III}M$, $L_{II, III} \rightarrow MM$, $L_{II, III} \rightarrow MM$. The same charge may be produced also by a smaller number of Auger processes accompanied by sudden perturbation excitation. The principal amount of $3s$ and $3p$ excitation accompanies the $K \rightarrow L_I L_I$ process; a very minor amount accompanies $L_{II, III} \rightarrow MM$. Substituting in Eq. (1) one obtains for M , with no sudden perturbation excitation, for the $K \rightarrow L_I L_I$

* Research carried out under the auspices of the U. S. Atomic Energy Commission.

¹ E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, London, 1952).

² E. L. Feinberg, *J. Phys. (U.S.S.R.)* 4, 424 (1941); H. M. Schwartz, *J. Chem. Phys.* 21, 45 (1953); H. Primakoff and F. T. Porter, *Phys. Rev.* 89, 930 (1953).

³ M. L. Perlman and J. Miskel, *Phys. Rev.* 91, 182 (1954); S. Wexler and T. H. Davies, *Phys. Rev.* 93, 182 (1954).

⁴ O. Kofoed-Hansen, *Phys. Rev.* 96, 1045 (1954); A. H. Snell and F. Pleasanton, *Phys. Rev.* 98, 1174(A) (1955).

⁵ J. C. Slater, *Phys. Rev.* 36, 57 (1930).

⁶ The hole nomenclature is employed here to designate Auger transitions.

transition,

$$M = \left| \int 1s_f^*(1)\alpha(1)F^*(2)\beta(2)1s_f^*(3)\beta(3)2p_{of}^*(4)\alpha(4) \right. \\ \left. \times 2p_{of}^*(5)\beta(5) \cdots \times \sum_{s>i} \frac{e^2}{r_{sj}} \sum_{\nu} (-1)^{\nu} P_{\nu} 2s_i(1)\alpha(1) \right. \\ \left. \times 2s_i(2)\beta(2)1s_i(3)\beta(3)2p_{oi}(4)\alpha(4)2p_{oi}(5)\beta(5) \cdots d\tau \right|^2, \quad (2)$$

where α and β refer to the two types of spin functions, F stands for the wave function of the ejected electron, P_{ν} represents the permutation of electrons, and ν is even or odd according to whether the permutation is even or odd. The quantity which is squared in Eq. (2) consists, when expanded, of a sum of terms, each of which is a product of a two-electron integral involving e^2/r_{sj} multiplied by a number of one-electron overlap-type integrals. Equation (2) reduces to

$$M = |A|^2 K, \quad (3)$$

with

$$A = \int 1s_f^*(1)\alpha(1)F^*(2)\beta(2) \\ \times \frac{e^2}{r_{12}} 2s_i(1)\alpha(1)2s_i(2)\beta(2) d\tau_1 d\tau_2$$

and

$$K = \left| \int 1s_f^* 1s_i d\tau \left(\int 2p_{fj}^* 2p_{id} d\tau \right)^6 \left(\int 3s_f^* 3s_i d\tau \right)^2 \right. \\ \left. \times \left(\int 3p_{fj}^* 3p_{id} d\tau \right)^6 - \left[6 \int 2p_{fj}^* 3p_{id} d\tau \int 3p_{fj}^* 2p_{id} d\tau \right. \right. \\ \left. \left. + \int 1s_f^* 3s_i d\tau \int 3s_f^* 1s_i d\tau \right] \times (\text{quantity of the} \right. \\ \left. \text{order unity}) + \text{smaller terms} \right|^2,$$

If one omits all terms not containing the two electron integral A , which is the e^2/r_{sj} integral corresponding to the Auger transition as it is usually taken. The terms involving other e^2/r_{sj} integrals are considered negligible, although this factor has not been thoroughly explored. The probability, M , of obtaining a final state with sudden perturbation excitation is similar to Eq. (3) with K suitably modified to indicate the orbitals which correspond to excitation in the final state. K , when summed over all possible final states for the electrons not taking part in the $K \rightarrow LL$ Auger transition, should be about equal to unity. This summed probability differs slightly from unity chiefly because transitions to $1s_f\alpha$ and $F\beta$ are not allowed.

Both $\int 1s_f^* 1s_i d\tau$ and $\int 2p_{fj}^* 2p_{id} d\tau$ are very close to unity, so that the deviation of K in Eq. (3) from unity gives the probability of the $3s$ and $3p$ electrons not

being in their original configuration. If one subtracts from this number the probability that the $3s$ electron makes a transition to the empty $2s$ orbital, one obtains the probability that the $3s$ and $3p$ electrons are actually excited during the Auger process. Integrals of the type appearing in Eq. (3) have usually been evaluated with hydrogenic atomic orbitals.² One finds, using Slater Z values and hydrogenic functions, that the probability of exciting $3s$ and $3p$ electrons in the foregoing Auger cascade leading to the plus five charged chlorine is 0.16; 98 percent of this total arises from the $K \rightarrow L_I L_I$ transition. Hydrogenic atomic orbitals are constructed in such a way that a $3s$ function corresponding to a given Z is orthogonal to a $2s$ function with the same value of Z . In the atom, the Z of the $2s$ function is of course different from that of the $3s$ function. The probability of excitation has therefore also been evaluated using Slater orbitals which are actually orthogonalized. The result obtained in this way for the excitation of $3s$ and $3p$ electrons is 0.12. While this number is close to that obtained with the hydrogenic functions, it should be noted that the bracketed quantity in the expression for K is negligible in the case of the orthogonal functions but is quite sizeable in the case of the hydrogenic functions.

Using hydrogenic functions, one finds that the probability of actually ionizing $3s$ and $3p$ electrons is only 0.03. However, some of the integrals computed here and calculations made by Levinger⁷ indicate that the ionization probability may be much higher than that computed with hydrogenic wave functions and, correspondingly, that the probability of excitation to bound states may be much lower. Moreover, the excited electrons may also take part in Coster-Kronig transitions of the type $M_I \rightarrow M_{II, III} X$, where X corresponds to the orbital to which the $3s$ or $3p$ electrons had been excited. How probable this Coster-Kronig transition may be compared with other processes which compete to fill the M_I hole or deexcite the X electron, one cannot easily say. One does know, however, that for outer shell orbitals radiative transitions are much less probable than Auger processes. Thus, under proper conditions, every excited $3s$ and $3p$ electron may be ionized, the result being the accumulation of a positive charge on the chlorine atom larger than five units, the maximum which may be produced by means of the usual Auger mechanisms following the creation of a K vacancy. Recent measurements by Snell and Pleasanton⁴ of the chlorine atom charge distribution show that there is 10 percent probability for Cl^{+5} , 1.8 percent for Cl^{+6} , and 0.4 percent for Cl^{+7} . Snell and Pleasanton's results indicate that some sudden perturbation "ionization" accompanies the Auger processes.⁸

⁷ J. S. Levinger, Phys. Rev. **90**, 11 (1953).

⁸ In a private communication, A. H. Snell has pointed out that these high charges may be produced also by the occurrence of Auger transitions $M_I \rightarrow M_{II, III} M_{II, III}$. It cannot be stated definitely that such transitions are energetically possible following the decay of A^{37} ; however, from the compilation of ionization

If one analyzes their results, assuming that the probability of sudden perturbation "ionization" is the same (except for a statistical factor) for all $K \rightarrow LL$ Auger processes (the main Auger processes for exciting $3s$ and $3p$ electrons), one finds that they are consistent with a probability of about 0.20 for exciting the $(3s)^2(3p)^6$ shell in the Auger cascade.⁹ This probability is of the

energies by Hill, Church, and Mihelich [Rev. Sci. Instr. 23, 523 (1952)], the indication is that these transitions may be exoergic.

⁹ This calculation was made on the basis that the probability of ionizing two electrons as a result of the sudden perturbation effect is just the square of the probability of ionizing one electron. This may be an oversimplification when the ionization proceeds

same order of magnitude as the one calculated above from theory. The theoretical value could change considerably, however, if more exact wave functions were available.

ACKNOWLEDGMENTS

The authors are greatly indebted to Dr. William Rubinson and to Dr. A. H. Snell for illuminating discussions on the subject of radiationless transitions.

by the mechanism $M_I \rightarrow M_{II,III}X$, since then the production of the plus seven charge requires a more severe restriction on the sequence of processes than the production of the plus six charge.

Correlation Energy of Helium

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(Received March 25, 1955)

The correlation energy of helium is calculated by using an approximate central potential, in a manner analogous to Slater's calculation of the exchange energy.

IN the Hartree self-consistent field equations for an n -electron atom of atomic number Z ,¹

$$\mathcal{H}u_i \equiv -\nabla_i^2 u_i - 2Z \frac{u_i}{r_i} + 2 \left[\sum' \int \frac{|u_k|^2}{r_{ik}} d\tau_k \right] u_i = \epsilon_i u_i, \quad (1)$$

(where atomic units have been used: $e^2 = 2$, $\hbar^2/2m = 1$), it is well known that the equation can be interpreted as a Schrödinger equation in which the third term on the left side is the interaction energy of each electron with an averaged-out, spherically symmetric charge distribution of all the other electrons. Thus ϵ_i is approximately the dissociation energy of the i th electron. In the sum $\sum \epsilon_i$, the interaction energies are taken into account twice; hence

$$E \equiv \langle H \rangle = \sum_i \epsilon_i - \sum_{i>k} \int \int \frac{|u_k|^2 |u_i|^2}{r_{ik}} d\tau_k d\tau_i, \quad (2)$$

where H is the Hamiltonian of the system, and the expectation value is taken with the Hartree function for the ground state,

$$\psi_H = u_1 u_2 \cdots u_n, \quad (3)$$

found from (1).

For helium, the Hartree-Fock function, which takes the symmetry of the wave function into account, is identical with the Hartree function, and $u_1 = u_2$, $\epsilon_1 = \epsilon_2 \equiv \epsilon$, so that² Eq. (2) yields

$$E_{He} = 2\epsilon - \int \int \frac{|u_1|^2 |u_2|^2}{r_{12}} d\tau_1 d\tau_2. \quad (4)$$

¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 677 ff., esp. Eq. (4), p. 677.

² Since the Hartree energy parameter $|\epsilon|$ has been assumed to be approximately equal to the first ionization potential, μ , then

Wilson and Lindsay³ calculated the Hartree $\psi(1s)$ function and its eigenvalue ϵ for helium, and found

$$\epsilon = -1.836 \text{ Rydbergs (ry)}, \quad E_{He} = -5.723 \text{ ry.}$$

This value is to be compared with the experimental value,

$$E_{exp} = -5.807 \text{ ry.}$$

[Note that according to reference 2, we indeed find $\epsilon - 4R_{He}/R_H = -5.836 \text{ ry.}$]

A self-consistent field calculation does not take into account, however, the instantaneous interactions among the electrons. These interactions give rise to a *correlation* in their positions (and hence a shift in the energy). For He in the ground state, the electrons have opposite spin so that there is no interaction between them due to the Fermi statistics, and the energy of correlation will arise solely from the Coulomb interaction. As good a definition of correlation energy as any, defines it as the difference between the energy as calculated from the Hartree-Fock procedure and the exact energy.⁴

Wigner⁵ has given a free-electron gas approximation to this correlation energy for alkali atoms in solids, in the form of an additional central "correlation" potential that the electrons of \pm spin are subject to, in the

in the ground state,

$$E_{\text{experimental}} = -\mu - \frac{Z^2 R_Z}{n^2 R_H} = -\mu - 4 \frac{R_{He}}{R_H} \sim \epsilon - 4 \frac{R_{He}}{R_H},$$

where the energy is, as before, in Rydbergs (ry).

³ V. C. Wilson and R. B. Lindsay, Phys. Rev. 47, 681 (1935).

⁴ See, however, Green, Mulder, and Miller, Phys. Rev. 91, 35 (1953); Green, Lewis, Mulder, Wyeth, and Woll, Phys. Rev. 93, 273 (1954).

⁵ E. Wigner, Phys. Rev. 46, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).