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Exchange corrections of K x-ray emission rates*

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Separate relativistic Hartree-Fock solutions for atoms in their initial and final states are used for calculating the radiative decay of a K-vacancy state. The matrix-element calculations include the exchange effects of the nonzero overlap of wave functions from different subshells. Results are presented for the filling of the vacancy by the p electrons for a set of elements from $Z=10$ to 98. The Hartree-Fock theory is also used for calculating the rates of production of multiple-vacancy states in the decay process. In contrast to earlier single-potential calculations, the calculated values of ratios of the rates of the K x-ray components are in good agreement with the experimental values.

INTRODUCTION

During the past several years a number of experimenters have measured the ratios of K-shell emission rates.[1,2] Experiments in which the K-shell vacancies have been produced by photoionization, electron ionization, and nuclear transitions should be only slightly influenced by the presence of multiple vacancies.[3] However, these experiments have shown a systematic deviation from theoretical results, based on a single-potential Hartree-Slater description of the atom.[4-7] In particular, the ratio of the $K\beta$ to $K\alpha$ x-ray components was measured to be of the order of 10% higher than the theoretical predictions.

In unpublished calculations, we have found little variation in the $K\beta/K\alpha$ ratio that is due to changes in the potential for single-potential calculations; use of the present Hartree-Fock wave functions without the overlap effects leads to an approximate 5% lowering of the $K\beta/K\alpha$ ratio.

A similar discrepancy had existed in the L/K electron-capture ratio.[8] This discrepancy was resolved by taking into account the exchange effects introduced by the change of the atomic wave functions in going from a nucleus to its daughter.

The situation in the radiative decay is very similar to that of electron capture.[9] In the case of the radiative decay, an outer electron filling the K-shell vacancy causes the change in the potential. Instead of the s electrons, which are of interest in the electron capture case, the p-shell electrons are mainly of interest here. For example, in considering the decay of a $3p$ electron, the overlap between the initial $3p$ state and the final $2p$ state is at most of the order of a few percent. The $2p$ state, however, has a much larger matrix element for decay to the $1s$ state, and the exchange correction thus gives rise to fairly large corrections.

To include the exchange correction in the calculation of the decay rates, separate relativistic Hartree-Fock calculations were made for the initial state with a vacancy in the $1s$ subshell, and for the final state with a vacancy in a p subshell. We then calculated the transition rate using the relativistic analog of the velocity form of the matrix element. The full determinant form of the wave functions was used in calculating the matrix elements.

Bagus[10] has previously calculated the transition matrix elements for 10- and 18-electron atoms, as is done here, using separate solutions of the Hartree-Fock equations and the complete expressions for the matrix elements.

In addition to calculating the rates for the transitions which leave a single vacancy in the atom, we have also calculated the rates for the transitions accompanied by excitations of other electrons in the atom.

RELATIVISTIC HARTREE-FOCK EQUATIONS

The "restricted" version of the Hartree-Fock formulism is used for the present calculations; that is, the radial wave functions of all the single-particle states of a given subshell are assumed to be identical. The integrodifferential eigenvalue equations are transformed to finite difference equations for the radial wave functions specified at a fixed set of radial distances. Essentially the same treatment of the relativistic Hartree-Fock equations as that used here has been described in recent papers of Desclaux *et al.*[11] and of Mann and Waber.[12] Reference is made to these papers for additional details and earlier references.

In the Hartree-Fock treatment, the N-particle wave function of an atom is assumed to be the asymmetrized sum of products of single-particle wave functions

$$\psi = (N!)^{-1/2} \sum_{\text{permutations}} (-1)^P \prod_i \phi_{\alpha_i}(\vec{r}_i) ,$$

where α_i is a fixed set of occupied states. The single-particle wave functions here and in usual treatments are assumed to be an orthonormal set. In the relativistic case, the ϕ's are four-component spinors. With the standard representation of the Dirac matrices, the wave function for a given angular-momentum state can be written as

$$\phi_\kappa^\mu = \frac{1}{r} \begin{pmatrix} G(r)\chi_\kappa^\mu(\hat{r}) \\ iF(r)\chi_{-\kappa}^\mu(\hat{r}) \end{pmatrix},$$

with

$$\chi_\kappa^\mu(\hat{r}) = \sum_m C(l\tfrac{1}{2}j;\, \mu-m\, m) Y_{l,\mu-m}(\hat{r}) \chi_{1/2}^m$$

and $\chi_{1/2}^m$ the spin-$\frac{1}{2}$ spinors. The total angular momentum and principal orbital angular momentum are related to κ by

$$j = |\kappa| - \tfrac{1}{2}, \quad l = \kappa \text{ for } \kappa > 0 \text{ and } l = \kappa - 1 \text{ for } \kappa < 0.$$

If we assume the radial wave functions are the same for a given subshell, include only the Coulomb interaction between electrons, and average over the energies of the possible different configurations for partially filled subshells, the total energy of the atom is

$$\begin{aligned} E = {} & \sum_A N_A I_A + \frac{\alpha}{2} \sum_A N_A(N_A - 1) \\ & \times \left(R^0(AAAA) - \frac{1}{2} \frac{\omega_A}{(\omega_A - 1)} \sum_{k>0} \Gamma_{AkA} R^k(AAAA) \right) \\ & + \alpha \sum_{A<B} N_A N_B \left(R^0(ABAB) - \tfrac{1}{2} \sum \Gamma_{AkB} R^k(ABBA) \right). \end{aligned}$$

Denoting

$$Y_{AB}^k(r) = \int dr' \left(\frac{r_<^k}{r_>^{k+1}} \right) (G_A G_B + F_A F_B)_{r'} ,$$

then we have

$$R^k(ABCD) = \int dr\, Y_{BD}^k (G_A G_C + F_A F_C)_r .$$

The sums on A and B go over the occupied subshells. N_A is the number of electrons in the subshell and ω_A is the statistical weight,

$$\omega_A = 2j_A + 1 ,$$

$$I_A = \int dr \left[2F_A \left(\frac{d}{dr} + \frac{\kappa_A}{r} \right) G_A - 2F_A^2 + V_N (G_A^2 + F_A^2) \right]_r ,$$

in units with $\hbar = c = m = 1$. $V_N(r)$ is the potential due to the nucleus. For a point nucleus

$$V_N(r) = -Z\alpha/r ,$$

we have followed Mann and Waber[12] and used the charge distribution

$$\rho_N(r) = \rho_0 \{ 1 + \exp[(r - R)/a] \}^{-1} ,$$

with

$$R = 1.07 A_M^{1/3} \times 10^{-13} \text{ cm} ,$$

$$a = 0.55 \times 10^{-13} \text{ cm} ,$$

$$\tfrac{1}{2}\Gamma_{AkB} = (2l_A + 1)(2l_B + 1) \begin{pmatrix} k & l_A & l_B \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} k & l_A & l_B \\ \frac{1}{2} & j_B & j_A \end{pmatrix}^2 ,$$

or alternately,

$$\tfrac{1}{2}\Gamma_{AkB} = \begin{pmatrix} j_A & k & j_B \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2 ,$$

if $l_A + l_B + k$ is even, and is zero otherwise. The Hartree-Fock equations follow from the assumption that the total energy is stationary with respect to variations of the wave functions which remain as an orthonormal set. The resulting equations are

$$\left(\frac{d}{dr} + \frac{\kappa_A}{r} \right) G_A - (E_A + 2 - V_A) F_A = \frac{\alpha}{2} \sum_{B \neq A} N_B F_B \sum_k \Gamma_{AkB} Y_{AB}^k + \sum_{\substack{B \neq A \\ \kappa_B = \kappa_A}} \lambda_{AB} N_B F_B ,$$

$$\left(-\frac{d}{dr} + \frac{\kappa_A}{r} \right) F_A - (E_A - V_A) G_A = \frac{\alpha}{2} \sum_{B \neq A} N_B G_B \sum_k \Gamma_{AkB} Y_{AB}^k + \sum_{\substack{B \neq A \\ \kappa_B = \kappa_A}} \lambda_{AB} N_B G_B ,$$

with

$$V_A(r) = V_N(r) + \alpha \left(\sum_B N_B Y_{BB}^0(r) - Y_{AA}^0(r) - \frac{\omega_A(N_A - 1)}{2(\omega_A - 1)} \sum_{k>0} \Gamma_{AkA} Y_{AA}^k(r) \right) .$$

The Lagrange multipliers $\lambda_{AB} = \lambda_{BA}$ enter from the restriction that the states from different subshells are to be orthogonal. They may be taken as zero if both subshells are completely occupied. Otherwise, if the subshells are not equally occupied, we have

$$(N_A - N_B)\lambda_{AB} = \alpha\left(\frac{\omega - N_B}{\omega - 1}\right)\left[\left(\frac{1-\omega}{\omega}\right)R^0(BBBA) - \sum_{k>0}\tfrac{1}{2}\Gamma_{AkB}R^k(BBBA)\right]$$

$$-\alpha\left(\frac{\omega - N_A}{\omega - 1}\right)\left[\left(\frac{1-\omega}{\omega}\right)R^0(AAAB) - \sum_{k>0}\tfrac{1}{2}\Gamma_{AkB}R^k(AAAB)\right] .$$

For the very few cases treated here in which two incomplete shells had equal occupations, the λ's were taken equal to zero, while the orthogonality was forced.[13]

The occupation numbers used for the subshells were those for the neutral atom with an additional vacancy in the 1*s* state for the initial state, and in the appropriate *p* state for the final state. Subshells partially filled in the neutral atom are assumed to be occupied proportional to the statistical weights for the two states having the same *n* and *l* values, but different *j*'s. This was also done for the partially filled final *P* states when these were in either of the outer two shells having *P* electrons.

TRANSITION RATES

In the present treatment, the single-particle wave functions making up the initial and final states are not identical. There are thus nonzero overlap matrix elements between states from different subshells. For such wave functions, Löwdin[14] has given the matrix elements of a single-particle operator in terms of the matrix elements between the single-particle states and the cofactors of the determinant of the overlap integrals.

The overlap integrals are nonzero only between states having identical angular-momentum states. We denote the determinant formed from the overlap integrals between the occupied states of one fixed angular-momentum state λ as

$$D_\lambda = \det(\phi'_{n'\lambda} \mid \phi_{n\lambda}) .$$

The label λ here specifies both the κ value and the magnetic quantum number. The signed cofactor of D_λ is denoted by

$$D_\lambda(n'_1 n'_2 \cdots n'_m \mid n_1 n_2 \cdots n_m) ,$$

in which the rows labeled by $n'_1 n'_2 \cdots n'_m$ and the columns labeled by $n_1 n_2 \cdots n_m$ have been deleted from the determinant.

The matrix element of a single-particle operator J_{LM} between the antisymmetrized wave functions is given as

$$\left(\psi' \left| \sum_i J_{LM}^{(i)} \right| \psi\right) = \left(\prod_\lambda D_\lambda\right) \sum_{n_p n'_s} D_{s\mu_s}(n'_s \mid 1)$$

$$\times (n'_s s\,\mu_s \mid J_{LM} \mid n_p p\,\mu_p) D_{p\mu_p}(n'_p \mid n_p) .$$

The product over λ is to be taken over all the different occupied angular-momentum states except the two taking part in the transition, i.e., the two denoted here as $s\mu_s$ and $p\mu_p$, in which p is to denote one of the two sets of p states. The initial vacancy is in the state denoted as $1s\mu_s$ and the final in $n'_p p\mu_p$. Since these states are not considered occupied, the full determinants of the cofactors are actually not defined.

The factors coming from the angular and spin variable are just those coming from the single-particle wave functions. In the present calculation, we have used the relativistic equivalent of the velocity form of the *E*1 matrix elements for which the radial matrix element is

$$R_L(e) = \int \frac{dr}{kr}\left[(F_B G_A - G_B F_A)L(L+1)j_L(kr) + (\kappa_B - \kappa_A)(F_B G_A + G_B F_A) \times\left(r\frac{d}{dr} + 1\right) j_L(kr)\right] ,$$

with $L = 1$.

The other factors entering the expression for transition rates as well as the expression for the *M*2 matrix element are given in Ref. 4. The *M*2 decay mode of the $p_{3/2}$ states was included in the calculation. The x-ray energy used in the calculation was obtained as the difference in total energy of the initial and final states.

For a partially filled *p* subshell above the state in which the vacancy was left, a weighted average was formed between treating one electron in the same angular-momentum state as the vacancy and treating no electrons in the same state. In the very few cases of partially filled outer *s* subshells, the electron was treated as in the same state as the vacancy; in any case, the exchange correction from the *s* subshells is small.

Table I lists the calculated values for the transition rates for *p* electrons to fill a vacancy in the

1*s* state. The units are eV/$\hbar$, where 1 eV/$\hbar$ $= 1.519 \times 10^{15}$ sec^{-1} = 1/27.21 a.u.

Bagus[10] has carried out the calculation nonrelativistically using the length, velocity, and acceleration forms of the dipole matrix elements. In Table II we list his values for neon and argon converted to f values for the length and velocity forms, along with our values summed for the j values. The bulk of the difference of his velocity value and ours for argon is due to the relativistic effects.

PRODUCTION OF MULTIPLE VACANCY STATES

In the process of the emission of the *K* x ray, more than one vacancy may be produced in the atom. The low-frequency satellites have been observed.[15-17] Theoretical calculations of the relative rates have previously been carried out by Åberg[18] and by Sachenko *et al.*[19] The basis of their calculations is the same as the present calculation.

We wish to compute the sum of the rates for the outer electrons to be left in any state. To carry out the sum, we use the single-particle solutions of the Hartree-Fock equations to give us a complete set of states; then, assuming that the energy-dependent factors change little for the major contribution to the sum, closure is used for the single-particle states.

Since we are using the determinant form for

TABLE I. Calculated *K* x-ray emission rates in units of eV/$\hbar$ by decays of electrons from *p* subshells.

Z	$2p_{1/2}$	$2p_{3/2}$	$3p_{1/2}$	$3p_{3/2}$	$4p_{1/2}$	$4p_{3/2}$	5p	6p
10	0.00141	0.00281						
13	0.0053	0.0106	0.00007	0.00014				
14	0.0076	0.0151	0.00021	0.00042				
15	0.0106	0.0209	0.00047	0.00093				
16	0.0143	0.0283	0.00088	0.00175				
17	0.0188	0.0372	0.00152	0.0030				
18	0.0238	0.0472	0.00244	0.0048				
19	0.0305	0.0603	0.0035	0.0070				
20	0.0385	0.0761	0.0048	0.0096				
22	0.0593	0.1168	0.0077	0.0152				
23	0.0724	0.1424	0.0095	0.0188				
24	0.0876	0.1720	0.0112	0.0222				
25	0.1049	0.2058	0.0140	0.0276				
26	0.1248	0.2444	0.0167	0.0329				
28	0.1730	0.338	0.0234	0.0459				
29	0.2017	0.393	0.0269	0.0527				
30	0.2338	0.455	0.0319	0.0624				
32	0.309	0.600	0.0440	0.0862	0.00097	0.00187		
33	0.353	0.685	0.0514	0.1005	0.00193	0.0037		
34	0.401	0.777	0.0598	0.1169	0.0033	0.0064		
35	0.454	0.876	0.0687	0.1342	0.0052	0.0101		
36	0.512	0.988	0.0776	0.1518	0.0077	0.0150		
37	0.576	1.109	0.0887	0.1735	0.0102	0.0198		
38	0.646	1.241	0.1010	0.1975	0.0130	0.0253		
40	0.804	1.539	0.1297	0.2533	0.0186	0.0362		
42	0.990	1.888	0.1640	0.320	0.0248	0.0482		
47	1.599	3.02	0.2789	0.543	0.0477	0.0925		
50	2.080	3.89	0.372	0.722	0.0697	0.1356	0.0060	
51	2.263	4.22	0.407	0.790	0.0785	0.1529	0.0114	
54	2.883	5.34	0.527	1.022	0.1073	0.2100	0.0399	
56	3.36	6.20	0.621	1.204	0.1317	0.2581	0.0622	
60	4.51	8.21	0.845	1.636	0.1857	0.363	0.0807	
63	5.54	10.00	1.050	2.031	0.2344	0.458	0.0969	
64	5.93	10.66	1.127	2.178	0.2536	0.496	0.1107	
65	6.33	11.35	1.205	2.331	0.2712	0.529	0.1091	
68	7.66	13.61	1.469	2.840	0.334	0.651	0.1285	
70	8.67	15.28	1.666	3.22	0.381	0.742	0.1430	
72	9.77	17.09	1.884	3.64	0.435	0.849	0.1798	
73	10.36	18.06	2.000	3.86	0.464	0.907	0.2002	
74	10.97	19.06	2.120	4.10	0.495	0.969	0.2218	
78	13.71	23.45	2.653	5.13	0.636	1.250	0.317	
79	14.48	24.64	2.800	5.41	0.675	1.330	0.345	
80	15.27	25.88	2.952	5.71	0.716	1.413	0.380	
81	16.09	27.16	3.11	6.01	0.759	1.499	0.417	0.0060
82	16.95	28.49	3.27	6.34	0.803	1.591	0.457	0.0151
85	19.74	32.72	3.80	7.36	0.946	1.883	0.590	0.0636
90	25.15	40.68	4.79	9.34	1.221	2.469	0.852	0.1652
92	27.61	44.19	5.23	10.22	1.343	2.736	0.970	0.1779
96	33.07	51.77	6.19	12.16	1.610	3.33	1.232	0.2211
98	36.08	55.84	6.70	13.22	1.753	3.66	1.374	0.2319

the matrix elements, the sum over the single-particle states can include the occupied states. To find the results, the determinants are expanded in terms of the row involving the state over which the final state is being summed. If we use the fact that the initial single-particle states form an orthonormal set, then the sum of the overlap factors of the angular-momentum states that do not change in the transition is

$$\sum_{n_1' < n_2' < \cdots n_p'} D_\lambda^2 = \sum_{n_1 < n_2 < \cdots n_p} D_\lambda^2 (n_1' n_2' \cdots n_p' \,|\, n_1 n_2 \cdots n_p) \,,$$

the sum over the deleted initial states being over all possible combinations. The major term in the sum is the one in which the initial states in the cofactors are the same as the fixed final states. In the actual calculation, the only additional terms included were those in which one initial state was included in the cofactor that was summed over in the final states. These terms go as the square of the off-diagonal terms.

The same analysis can be carried through for the cofactors that involve the angular momenta that change in the transition. The calculation of the exact expression would require the calculations of additional matrix elements. We have approximated the sum as

$$\Big(\sum_{n_s' n_p} D_s(\cdots n_s' \,|\, \cdots 1s)(n_s' \,|\, J \,|\, n_p) D_p(\cdots n_p' \,|\, \cdots n_p) \Big)^2 + \sum_a \Big(\sum_{n_s' n_p} D_s(\cdots n_s' \,|\, \cdots 1s)(n_s' \,|\, J \,|\, n_p) D_p(\cdots n_p' \,|\, \cdots n_a^{-1} n_p' n_p) \Big)^2 - \sum_a \Big(\sum_{n_s' n_p} D_s(\cdots n_s' \,|\, \cdots 1s)(n_s' \,|\, J \,|\, n_p) D_p(\cdots \,|\, \cdots n_a^{-1} n_p) \Big)^2 \,.$$

For the s cofactor, the states summed over are deleted from the cofactor in both the initial and final states. For the p cofactor the states summed over are also deleted, except in the second and third terms, where the state n_a of the set summed over is included in the initial states. The first two terms include transitions in which there is an electron in the state n_p' in the final state, while the third term subtracts such transitions. This approximation neglects exchange contributions of excited s states and terms going as the square of the off-diagonal overlap integrals.

Table III lists the percentage of the rates summed for the satellite structure compared to the main line. The sum here was carried out to include multivacancies in the same shell as that from which the K-shell vacancy was filled, and in all outer shells. The rates have been summed for the two p subshells in a given shell. For high-Z elements, the relative probability of the production of multivacancies accompanying a decay from the L_3 subshell approaches a value of twice that for decays from the L_2 subshell. Figure 1 presents the percentage contributions as a function of Z. In Table IV the results are broken down according to the shell in which the second vacancy occurred. Åberg[18] gives values of 4.0% for the $K \rightarrow L^2$ in neon, and 0.51% for the $K - L^2$ and 7.3% for the $K \rightarrow M^2$ relative contributions in argon. These include an estimate of the correction due to the energy-dependent factors. Keshi-Rahhonen and Utrianen[17] have measured a 5% ratio for the $K \rightarrow M^2$ structure in argon. These values are not grossly different from those calculated here.

It should be noted that electron correlation effects have been found to be important in the process of double photoionization from the same subshell,[20,21] and are likely to be important in the emission process.

RESULTS

Table V lists the calculated values of the total decay rate in units of eV/$\hbar$ and emission-rate ratios of $K\beta/K\alpha$, $K\alpha_2/K\alpha_1$, $K\beta_3/K\beta_1$, $K\beta_1'/K\alpha_1$, and $K\beta_2'/K\alpha_1$. The $K\alpha_2/K\alpha_1$ and $K\beta_3/K\beta_1$ ratios given do not include the low-frequency satellite contributions; these ratios are little changed from the values calculated on the basis of the Hartree-Slater single-potential theory. In the total rate and the summed components $K\alpha$, $K\beta$, $K\beta_1'$, and $K\beta_2'$, we have included the rates for the production

TABLE II. f values from Bagus (Ref. 10) compared to the present calculation.

		Bagus		
		Length	Velocity	Present calculation
$Z=10$	$2p-1s$	0.2280	0.2058	0.2043
$Z=18$	$3p-1s$	0.02727	0.02536	0.02497
	$2p-1s$	0.3012	0.2895	0.2838

of the multivacancy states and have also added the rates of decay of the electrons from *s*, *d*, and *f* states. These latter transitions go by $E2$, $M1$, and $M2$ transitions, and were calculated by the Hartree-Slater theory.[4] $K\beta_1'$ denotes the M-to-K transitions, and $K\beta_2'$ all transitions from shells above the M.

In Fig. 2 the theoretical values for the $K\beta/K\alpha$ ratio on the basis of the present Hartree-Fock calculation and the earlier single-potential Hartree-Slater potential are plotted with the experimental data.[22-32] In Fig. 3 the results for the $K\beta_2'/K\alpha_1$ ratio are plotted.

The present total decay rates range from 10% larger than the previous single-potential values for the low-Z elements, to 2% larger for the high-Z elements.

TABLE III. Percentage rate of production of multivacancy states relative to single-vacancy production.

Z	$2p$	$3p$	$4p$	$5p$	$6p$
10	4.35				
13	2.33	5.78			
14	1.89	7.50			
15	1.60	8.05			
16	1.41	8.09			
17	1.35	7.98			
18	1.47	7.77			
19	1.32	6.55			
20	1.18	5.61			
22	1.04	5.13			
23	0.97	4.86			
24	0.94	4.79			
25	0.82	4.37			
26	0.76	4.15			
28	0.66	3.76			
29	0.63	3.63			
30	0.57	3.43			
32	0.46	3.11	3.99		
33	0.42	2.91	4.56		
34	0.40	2.76	4.88		
35	0.39	2.69	5.04		
36	0.36	2.70	5.15		
37	0.34	2.58	4.52		
38	0.33	2.45	4.07		
40	0.31	2.21	4.29		
42	0.30	1.98	4.52		
47	0.24	1.57	4.15		
50	0.22	1.35	3.69	3.29	
51	0.21	1.30	3.51	3.83	
54	0.19	1.19	3.33	4.55	
56	0.18	1.13	3.10	3.74	
60	0.22	1.31	2.69	2.24	
63	0.22	1.28	2.45	1.78	
64	0.20	1.16	2.39	2.17	
65	0.23	1.27	2.33	1.60	
68	0.21	1.18	2.15	1.31	
70	0.22	1.17	2.06	1.26	
72	0.18	0.97	1.95	1.75	
73	0.17	0.92	1.91	1.92	
74	0.16	0.87	1.88	2.07	
78	0.14	0.75	1.74	2.50	
79	0.14	0.72	1.70	2.54	
80	0.14	0.70	1.68	2.51	
81	0.14	0.71	1.63	2.53	1.54
82	0.13	0.68	1.58	2.44	2.48
85	0.13	0.63	1.51	2.33	3.50
90	0.12	0.58	1.40	2.24	3.37
92	0.13	0.63	1.40	2.20	2.24
96	0.13	0.63	1.32	2.09	1.68
98	0.14	0.65	1.30	2.05	1.20

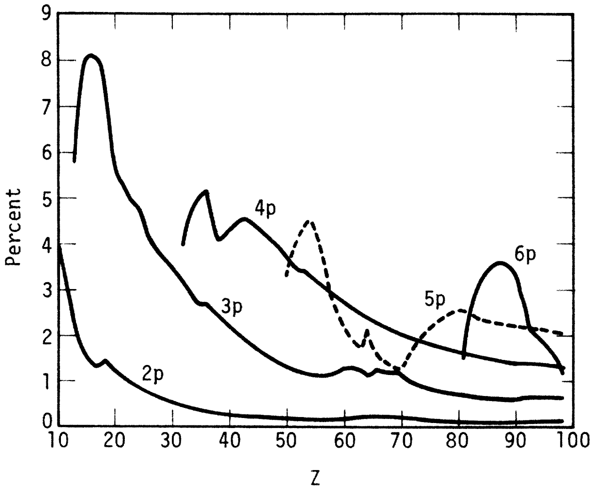

FIG. 1. Calculated percentage rate for the production of multivacancies accompanying the decay from the designated *p* states relative to single-vacancy production rate, as a function of atomic number.

TABLE IV. Percentage rates of production of second vacancy relative to the transition rate of the main line.

Z	K-L^2	K-LM	K-LN	K-LO	
10	4.35				
18	0.71	0.76			
26	0.28	0.46	0.024		
36	0.10	0.18	0.079		
40	0.078	0.140	0.089	0.0060	
54	0.038	0.075	0.050	0.031	
	K-M^2	K-MN	K-MO	K-N^2	K-NO
18	7.73				
26	4.07	0.078			
36	2.11	0.59		5.15	
40	1.55	0.63	0.021	4.09	0.20
54	0.55	0.52	0.12	2.72	0.61

DISCUSSION

With the inclusion of the exchange correction in the theoretical results, the systematic discrepancy between theory and experiment has been removed. Any remaining discrepancies are at present within the spread of the experimental values.

We have used the occupation numbers for the neutral atoms and the irregularities occurring such as at $Z=24$, 29, 57, and 64 are reflected in our values. The treatment here of the valence shell is crude, even as representing neutral atoms. The experiments have in general been carried out with metals, and smoothly varying fractional occupations should be more appropriate. It is not surprising then that the irregularities are not present in the measurements.

Within the Hartree-Fock formalism, more-complete calculations can be carried out by using different radial wave functions even within a single subshell, and by dealing with particular angular-momentum couplings.

The approach taken in the present paper is to use the Hartree-Fock formalism as a prescription for the calculation of wave functions. By using separate solutions for the initial and final states,

TABLE V. Total K-vacancy decay rate in units of eV/$\hbar$ and ratios of x-ray components as a function of Z.

Element	Z	Total (eV/$\hbar$)	$K\beta/K\alpha$	$K\alpha_2/K\alpha_1$	$K\beta_3/K\beta_1$	$K\beta'_1/K\alpha_1$	$K\beta'_2/K\alpha_1$
Ne	10	0.0044		0.5028			
Al	13	0.0165	0.0134	0.5033	0.5057	0.0201	
Si	14	0.0238	0.0294	0.5037	0.5052	0.0443	
P	15	0.0335	0.0472	0.5048	0.5048	0.0710	
S	16	0.0461	0.0659	0.5053	0.5047	0.0992	
Cl	17	0.0616	0.0862	0.5056	0.5041	0.1298	
Ar	18	0.0799	0.1088	0.5049	0.5041	0.1638	
K	19	0.1032	0.1211	0.5055	0.5042	0.1824	
Ca	20	0.1312	0.1315	0.5061	0.5043	0.1982	
Ti	22	0.2020	0.1355	0.5076	0.5054	0.2043	
V	23	0.2464	0.1367	0.5083	0.5060	0.2063	
Cr	24	0.2970	0.1337	0.5091	0.5070	0.2018	
Mn	25	0.357	0.1385	0.5099	0.5073	0.2092	
Fe	26	0.424	0.1391	0.5107	0.5079	0.2102	
Ni	28	0.586	0.1401	0.5124	0.5093	0.2119	
Cu	29	0.681	0.1379	0.5133	0.5105	0.2087	
Zn	30	0.790	0.1410	0.5142	0.5108	0.2135	
Ge	32	1.051	0.1504	0.5149	0.5105	0.2229	0.0049
As	33	1.204	0.1560	0.5153	0.5113	0.2277	0.0086
Se	34	1.375	0.1624	0.5158	0.5116	0.2331	0.0131
Br	35	1.560	0.1683	0.5181	0.5116	0.2372	0.0183
Kr	36	1.766	0.1727	0.5186	0.5111	0.2381	0.0240
Rb	37	1.992	0.1780	0.5195	0.5113	0.2423	0.0281
Sr	38	2.239	0.1831	0.5205	0.5115	0.2463	0.0320
Zr	40	2.800	0.1913	0.5225	0.5120	0.2543	0.0370
Mo	42	3.46	0.1981	0.5247	0.5125	0.2617	0.0403
Ag	47	5.61	0.2130	0.5305	0.5138	0.2775	0.0484
Sn	50	7.32	0.2230	0.5343	0.5148	0.2857	0.0564
Sb	51	7.97	0.2266	0.5356	0.5151	0.2882	0.0597
Xe	54	10.19	0.2368	0.5398	0.5157	0.2951	0.0695
Ba	56	11.91	0.2433	0.5428	0.5160	0.2997	0.0756
Nd	60	15.93	0.2504	0.5491	0.5167	0.3086	0.0792
Eu	63	19.55	0.2549	0.5542	0.5170	0.3147	0.0813
Gd	64	20.89	0.2570	0.5559	0.5171	0.3166	0.0832
Tb	65	22.28	0.2575	0.5577	0.5171	0.3185	0.0826
Er	68	26.88	0.2612	0.5634	0.5174	0.3240	0.0843
Yb	70	30.32	0.2634	0.5673	0.5175	0.3274	0.0853
Hf	72	34.09	0.2666	0.5714	0.5176	0.3307	0.0883
Ta	73	36.10	0.2682	0.5736	0.5176	0.3323	0.0898
W	74	38.20	0.2698	0.5757	0.5176	0.3338	0.0913
Pt	78	47.50	0.2758	0.5850	0.5173	0.3399	0.0972
Au	79	50.06	0.2772	0.5874	0.5172	0.3414	0.0987
Hg	80	52.72	0.2788	0.5899	0.5170	0.3430	0.1004
Ti	81	55.49	0.2804	0.5924	0.5167	0.3444	0.1023
Pb	82	58.37	0.2821	0.5950	0.5165	0.3459	0.1043
At	85	67.67	0.2873	0.6033	0.5158	0.3503	0.1105
Th	90	85.47	0.2952	0.6182	0.5134	0.3577	0.1205
U	92	93.41	0.2975	0.6247	0.5122	0.3606	0.1233
Cm	96	110.81	0.3019	0.6387	0.5090	0.3665	0.1290
Cf	98	120.29	0.3037	0.6462	0.5070	0.3695	0.1315

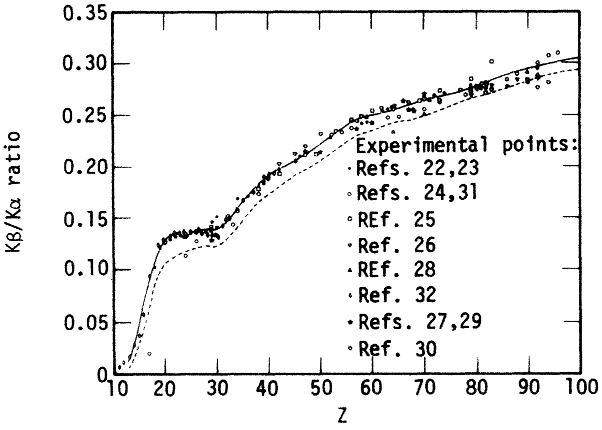

FIG. 2. The $K\beta/K\alpha$ radiative transition rate ratio as a function of atomic number. The solid curve is from the present calculated values; the dashed curve is calculated on the basis of the Hartree-Slater single-potential theory (Ref. 4).

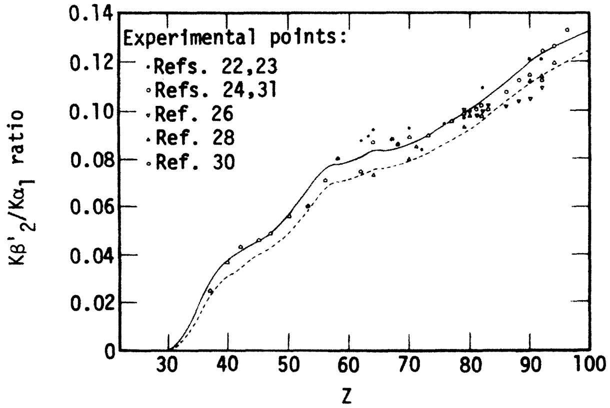

FIG. 3. The $K\beta_2'/K\alpha_1$ radiative transition rate ratio as a function of atomic number.

excellent agreement has been obtained with the experimental results. On the one hand, the exchange contribution should be examined in all the inner-shell transition processes; on the other hand, calculations giving these results within the framework of a systematic development are desirable.

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[1] Recent reviews have been given by Bambynek, Crasemann, Fink, Freund, Mark, Swift, Price, and Rao, in Rev. Mod. Phys. 94, 716 (1972); and by S. I. Salem, in Ref. 2. p. 285.

[2] Inner-Shell Ionization Phenomena and Future Applications, Proceedings of the Atlanta Conference, edited by R. W. Fink, S. T. Manson, J. M. Palms, and P. Venugopala Rao, U. S. Atomic Energy Commission Report No. CONF-720404, 1973 (unpublished).

[3] Estimates of probabilities of production of the multi-ionized atoms are given in the reviews of T. Åberg, p. 1509 of Ref. 2 and of M. O. Krause, p. 1587 of Ref. 2. Except for weakly-bound electrons, the rates, per electron in the upper state and per vacancy in the lower, are little influenced by the actual occupations. The effects of multivacancies thus come about mainly due to the different occupations.

[4] J. H. Scofield, Phys. Rev. 179, 9 (1969). Results for all elements from $Z=5$–102 are available in UCRL-51231 (unpublished).

[5] H. R. Rosner and C. P. Bhalla, Z. Phys. 231, 347 (1970).

[6] E. J. McGuire, Phys. Lett. A 33, 288 (1970).

[7] C. C. Lu, F. B. Malik, and T. A. Carlson, Nucl. Phys. A 175, 289 (1971).

[8] See the reviews of F. Vatai, p. 1957 of Ref. 2, and Harold Genz, p. 1965 of Ref. 2.

[9] The question as to whether the discrepancy between experiment and theory could be due to the exchange correction was put to the author by B. Craseman in 1969.

[10] P. S. Bagus, Phys. Rev. 139, A619 (1965), and Argonne National Laboratory Report No. ANL-6959 (1964).

[11] J. P. Desclaux, D. F. Mayers, and F. O'Brien, J. Phys. B 4, 631 (1971).

[12] J. B. Mann and J. T. Waber, At. Data, 5, 201 (1973).

[13] For a discussion of the effects of the off-diagonal multipliers, see Ref. 10. Charlotte Froese Fischer, Can. J. Phys. 45, 7 (1967) and 46, 2435 (1968), has looked at different approaches to the problem in which incomplete shells have equal occupations.

[14] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

[15] See the review of P. E. LaVilla, Ref. 2, p. 509 and references therein.

[16] L. O. Werme, B. Grennberg, J. Nordgren, C. Nordling, and K. Siegbahn, Phys. Lett. A 41, 113 (1972).

[17] O. Keshi-Rahkonen and J. Utriainen, Comment. Phys. Math (Finland) 42, 297 (1973).

[18] T. Åberg, Phys. Rev. A 4, 1735 (1971).

[19] V. P. Sachenko, A. V. Vedrinski, J. Richter, and V. V. Krivitski, Izv. Akad. Nauk SSSR, Ser. Fiz. 36, 226 (1972). [Bull. Acad. Sci. USSR, Phys. Ser. 36, 209 (1972)].

[20] F. W. Byron and C. J. Joachain, Phys. Rev. 164, 1 (1967).

[21] T. N. Chang, T. Ishihura, and R. T. Poe, Phys. Rev. Lett. 27, 838 (1971).

[22] V. W. Slivinsky and P. J. Ebert, Phys. Lett. A 29, 463 (1969); Phys. Rev. A 5, 1581 (1972).

[23] P. J. Ebert and V. W. Slivinsky, Phys. Rev. 188, 1 (1969).

[24] J. S. Hansen, H. U. Freund, and R. W. Fink, Nucl. Phys. A 142, 604 (1970); Nucl. Phys. A 153, 465 (1970).

[25] L. M. Middleman, R. L. Ford, and R. Hofstadter, Phys. Rev. A 2, 1429 (1970).

[26] A. G. dePinho, Phys. Rev. A 3, 905 (1971).

[27] V. D. Mistry and C. A. Quarles, Nucl. Phys. A 164,

219 (1971).

[28] O. W. B. Schult, Z. Naturforsch. A 26, 368 (1971).

[29] V. D. Mistry and C. A. Quarles, Phys. Lett. A 36, 221 (1971).

[30] J. H. McCrary, L. V. Singman, L. H. Zeigler, L. D. Looney, C. M. Edmonds, and Carolyn E. Harris, Phys. Rev. A 4, 1745 (1971).

[31] W. D. Schmidt-Ott, J. S. Hansen, and R. W. Fink, Z. Phys. A 250, 191 (1972); W. D. Schmidt-Ott, F. Tolea, and R. W. Fink, p. 338 of Ref. 2.

[32] S. I. Salem, T. H. Falconer, and R. W. Winchell, Phys. Rev. A 6, 2147 (1972).