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Slater's Transition State Concept for the X-Ray Emission Rate

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The Slater's concept for the use of fractional electron occupation numbers has been tested for x-ray transition probabilities. The K x-ray emission rates have been calculated with the relativistic Hartree-Fock-Slater wave functions in the transition-state method. The numerical results are compared with those with the conventional frozen-orbital method and with the Hartree-Fock calculations of Scofield including the exchange correction. It is found that the transition-state method increases the x-ray emission rates and improves the total radiative widths, but cannot explain the experimental data of K_β/K_α x-ray intensity ratios.

KEY WORDS: X-Ray Emission Rate / Transition State / K X-Ray Intensity Ratio /

I. INTRODUCTION

In recent years, there have been reported many theoretical calculations of x-ray emission rates using realistic atomic wave functions, such as the self-consistent-field wave functions.[1] Most of these calculations have been performed with the relativistic Hartree-Fock-Slater (RHFS) model. It is usual to use the same atomic potential for the initial and final states, i.e. the *frozen-orbital* approximation. The calculated values have been successfully adopted to interpret experiment. However, the experimental K_β/K_α x-ray intensity ratios have been found to be about 10% higher than the theoretical values.

This discrepancy has been resolved by Scofield.[2] Taking into account the presence of the vacancy, he used different atomic potentials for initial and final states, i.e. the *relaxed-orbital* approximation, and included the exchange effect between different subshells due to the imperfect overlap of the atomic wave functions. The calculated values with the relativistic Hartree-Fock (RHF) wave functions are in good agreement with the measured K_β/K_α ratios.

On the other hand, Slater *et al.*[3-5] have shown that when Slater's statistical approximation is used for the exchange term in the Hartree-Fock (HF) model, the energy eigenvalues have not the same physical meaning as the HF ones, but are partial derivatives of the total energy with respect to the orbital occupation numbers. Accordingly the energy eigenvalues do not agree well with the experimental ionization energies and the Koopmans' theorem cannot be used.

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In order to obtain the ionization energy by the use of the Slater's approximation, Slater[5] proposed a concept of the transition state in which one-half of an electron is removed from the atomic orbital concerned. The energy eigenvalues for atomic orbitals with fractional electron occupation numbers have proved to give correct ionization energies.[6~8] This is because the orbital relaxation effects are taken into consideration in the transition-state concept.

As an application of the idea of the transition-state method, Slater pointed out the possibility for calculations of transition probabilities in atoms.[9] When an atomic electron makes a transition, we assume that this electron stays half in the initial state and half in the final state.

The concept of the transition state has often been used to calculate x-ray emission rates in atoms and molecules. However, in contrast to the case for energy eigenvalues, the transition-state method for transition probabilities has not yet been tested in detail. The great advantage of this method consists in the fact that the transition-state method is a kind of the relaxed-orbital approximation, but the exchange effect does not exist because of orthogonality of atomic wave functions. In the present work, we use the transition-state concept for the calculation of K x-ray emission rates. The calculated results are compared with those from other theoretical models and the validity of the transition-state method for x-ray emission rates is discussed.

II. THEORETICAL MODEL

The calculations have been made using the RHFS computer program, which is equivalent to the program of Liberman, Cromer, and Waber.[10] In the RHFS method, the choice of the statistical exchange parameter α is important. Several attempts to determine this parameter have been reported and the values between 2/3 and 1 have usually been used. Schwarz[11] estimated the optimal value of this parameter for the ground state of atoms. According to his results, the optimal values are very close to 0.7 for atoms with $Z \geqq 10$. We have shown that the K x-ray emission rate increases with increasing α, about 3% between $2/3 \geqq \alpha \geqq 1$.[12] For practical purposes, it is enough to use the value of 0.7 except for very light elements. All the calculations in the present work have been performed with $\alpha = 0.7$.

In the RHFS calculations, the electron occupation numbers of the atomic orbitals corresponding to the initial and final vacancies are reduced by 0.5. The x-ray transition energy is obtained as the difference between the energy eigenvalues of these two orbitals. The K x-ray energies thus calculated are slightly larger than those obtained from the Dirac-Fock-Slater model including full relaxation and QED corrections.[13] The difference is almost constant for different K x-ray transitions in the same element, about 2% for Cu and less than 1.5% for $Z \geqq 50$. The different RHFS calculations were made for different pairs of atomic orbitals corresponding to the radiative transitions.

The x-ray emission rates have been obtained by the use of the formulation of Scofield.[14] All multipole contributions fo the radiation field as well as the retardation effect are included.

III. RESULTS AND DISCUSSION

The numerical results of x-ray emission rates for a K-shell vacancy are listed in Table I for Cu, Sn, Au, and U. In order to compare with the present results, the RHFS values of Scofield[15] in the frozen-orbital (FO) approximation with $\alpha=1$ and the RHF values[2] with the exchange effect are also shown. It can be seen from the table that the transition-state (TS) values are larger than the FO ones and close to the RHF values with exchange. For transitions from L subshells, the TS values are in good agreement with the RHF values. However, in the case of the transitions from the shells outer than the M shell the TS values are still smaller than the RHF values.

In Table II, the K_β/K_α ratios and the total radiative widths are listed. It is clear that the K_β/K_α ratio does not change by the use of the transition-state concept, or

Table I. Comparison of K x-ray emission rates, in units of (eV/h).

Z	Model	L_2	L_3	M_2	M_3	N_2	N_3	$O_{2,3}$	$P_{2,3}$
29	FO[a]	0.1942	0.3788	0.0235	0.0460				
	TS[b]	0.2024	0.3944	0.0244	0.0477				
	RHF[c]	0.2017	0.393	0.0269	0.0527				
50	FO	2.047	3.831	0.3460	0.6707	0.0626	0.1211	0.0040	
	TS	2.096	3.917	0.3514	0.6807	0.0645	0.1244	0.0052	
	RHF	2.080	3.89	0.372	0.722	0.0697	0.1356	0.0060	
79	FO	14.36	24.43	2.688	5.201	0.6305	1.232	0.3112	
	TS	14.58	24.76	2.717	5.244	0.6373	1.240	0.3356	
	RHF	14.48	24.64	2.800	5.41	0.675	1.300	0.345	
92	FO	27.42	43.88	5.060	9.894	1.266	2.561	0.9094	0.1529
	TS	27.79	44.36	5.106	9.960	1.276	2.570	0.9180	0.1549
	RHF	27.61	44.19	5.23	10.22	1.343	2.736	0.970	0.1779

[a] Reference 15.
[b] Present result.
[c] Reference 2.

Table II. Comparison of K_β/K_α ratio and total radiative width (eV).

Z		FO[a]	TS[b]	RHF[c]
29	K_β/K_α	0.1213	0.1208	0.1379
	Γ	0.643	0.669	0.681
50	K_β/K_α	0.2062	0.2053	0.2230
	Γ	7.09	7.25	7.32
79	K_β/K_α	0.2648	0.2640	0.2772
	Γ	49.1	49.7	50.06
92	K_β/K_α	0.2866	0.2854	0.2975
	Γ	91.8	92.8	93.41

[a] Reference 15.
[b] Present result.
[c] Reference 2.

becomes even worse. On the other hand, the transition-state method increases the total radiative widths, but the obtained values are still smaller in comparison with the RHF values.

In conclusion, we have shown that the use of the Slater's transition-state concept increases the K x-ray emission rates, but cannot reproduce the RHF values of Scofield with exchange effect, which are in agreement with the experimental data. This fact means that the transition-state method is very useful to calculate the quantities, where the relaxation effects are important, but insufficient for the phenomena, in which the exchange effect plays an important role. It should be noted also that the electron shakeoff process accompanying the x-ray emission[16] cannot be explained by the transition-state concept.

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