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Statistical Exchange Parameter and X-Ray Emission Rates

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The effect of choice of the statistical exchange parameter α on the x-ray emission rate has been studied by the use of the relativistic Hartree-Fock-Slater method. The finite nuclear size effect and the retardation effect are taken into account. It is found that the K x-ray emission rate increases with increasing α . The difference between the emission rates with $\alpha=2/3$ and $\alpha=1$ is less than 3.2% for transitions studied here.

KEY WORDS: Statistical exchange parameter/ K x-ray emission rate/
Relativistic Hartree-Fock-Slater method/

1. INTRODUCTION

Although the Hartree-Fock (HF) method is the most realistic model for atomic structure calculations, the solution of the HF equations is complex and time-consuming even for modern high-speed computers. This is mainly due to the exchange terms appeared in the HF equations. In order to overcome this difficulty, Slater¹⁾ proposed the approximation that the exchange terms be replaced by an average exchange potential. This method, called the Hartree-Fock-Slater (HFS) method or the $X\alpha$ method, reduces the original integro-differential equation to a series of one-electron Schrödinger equations. Owing to this simplicity, the HFS method has been widely used for atomic and molecular calculations.^{2,3)}

The Slater exchange term is proportional to the cubic root of the electron density and contains an adjustable parameter α . In the original paper of Slater,¹⁾ this statistical exchange parameter was taken to be unity. Subsequently, in order to achieve better agreement with experiment, attempts have been made to determine this parameter in a variety of ways. For example, Gáspár⁴⁾ and Kohn and Sham⁵⁾ proposed to use $\alpha=2/3$.

Schwarz⁶⁾ estimated the *optimal* values of α for the ground state of atoms from $Z=2$ to 86 in two different ways: (1) The statistical total energy is equal to the HF energy and (2) the virial theorem is satisfied. Both conditions give the values of α in close agreement with each other for all elements, which lie in the range of $2/3 \leq \alpha \leq 1$. For $Z \geq 3$, they decrease with increasing Z and it is a good approximation to adopt $\alpha=0.7$ except for light elements.

On the other hand, Gáspár⁷⁾ suggested an *ab initio* method to determine the statis-

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tical exchange parameter. His method gives the different values of α for different atomic shells. The α value for the overall atom can be obtained by an averaging procedure with an appropriate weight function. Gáspár and Nagy⁸⁾ tested the expectation values of powers of the radial distance, $\langle \frac{1}{r} \rangle$, $\langle r \rangle$, and $\langle r^2 \rangle$, for various values α by the use of the HFS method. According to their results, the Gáspár's method as well as the value of Schwarz gives the expectation values in good agreement with the HF calculations.

Recently, Band *et al.*⁹⁾ estimated the effect of choice of α on the internal conversion coefficient (ICC) of nuclear decay when it is calculated by the RHFS method. They found that the difference between the ICC's with $\alpha=1$ and with $\alpha=2/3$ increases when the transition energy becomes lower and when the multipolarity of the transition becomes higher. For 10-keV or M4 transitions, the difference is a few percent.

The relativistic HFS (RHFS) model has been used for the x-ray emission rate calculations of Scofield,¹⁰⁾ Rosner and Bhalla,¹¹⁾ Bhalla,¹²⁾ and Lu *et al.*¹³⁾ All these calculations used the value of $\alpha=1$. However, up to present there has been reported no study of the influence of the value of α on the x-ray emission rate. It is the purpose of the present work to estimate how much changes the x-ray emission rate by changing the statistical exchange parameter in the RHFS model.

2. METHOD OF CALCULATION

The relativistic x-ray emission rate can be calculated in the manner similar to the method used in the M-shell x-ray emission rates,¹⁴⁾ except for the value of the statistical exchange parameter. Therefore only brief description is given here.

In the HFS model, the exchange potential is given by

$$V_{ex} = -6\alpha e^2 [3/8\pi\rho(r)]^{1/3}, \quad (1)$$

where α is the statistical exchange parameter, e is the electric charge, $\rho(r)$ is the charge density and r is the radial distance from the center of the atom. Using Eq. (1), the RHFS calculations are made by the computer code, which is equivalent to the program of Liberman *et al.*¹⁵⁾ The effect of the finite nuclear size is taken into consideration by assuming the nucleus as a uniformly charged sphere.

According to the formulation of Scofield,¹⁰⁾ the x-ray emission rate can be written by

$$F = 2e^2\omega^2 \sum [f_L(m) + f_L(e)], \quad (2)$$

where ω is the energy of the emitted photon. The relativistic units ($\hbar=m_e=c=1$) are used. The oscillator strengths $f_L(m)$ and $f_L(e)$ are defined as

$$f_L(m) = B(-k_i, k_f, L) R_L^2(m)/\omega, \quad (3)$$

and

$$f_L(e) = B(k_i, k_f, L) R_L^2(e)/\omega. \quad (4)$$

Here $B(k_i, k_f, L)$ is the angular coupling coefficients, L is the multipolarity, $R_L(m)$ is

the radial matrix element for magnetic transition, $R_L(\theta)$ is that for electric transition, and k_i and k_f are the relativistic quantum numbers for initial and final states, respectively.

The explicit expressions for the angular coupling coefficients and for the radial matrix elements and the method to calculate the x-ray transition energies are given in Ref. 14.

In the present work, we used the so-called *frozen-orbital* approximation, i. e. the same atomic potential is used for initial and final states. The RHFS calculations are made for the ground-state configuration of neutral atoms.

3. RESULTS AND DISCUSSION

The numerical calculations for x-ray emission rates of a K-shell vacancy have been performed for $Z=29$, 50, 79, and 92. The electron transitions from L and M shells were considered and the contributions from all multipoles were included. All the calculations were made on the FACOM M-382 computer in the Data Processing Center of Kyoto University.

The calculated results of the K x-ray emission rates for $\alpha=2/3$, 0.7, and 1.0 are presented in Table 1. The present values with $\alpha=1$ coincide with the tabulated values of Scofield.¹⁰ It can be seen from the table that for all transitions in all elements the x-ray emission rate increases with increasing α .

Table 1. K x-ray emission rates (eV/ \hbar).

Z	Shell	$\alpha=2/3$	$\alpha=0.7$	$\alpha=1.0$
29	L ₂	0.1880	0.1886	0.1942
	L ₃	0.3666	0.3678	0.3788
	M ₂	0.0228	0.0229	0.0235
	M ₃	0.0446	0.0448	0.0460
50	L ₂	2.013	2.016	2.047
	L ₃	3.766	3.772	3.831
	M ₂	0.3365	0.3375	0.3460
	M ₃	0.6522	0.6540	0.6707
79	L ₂	14.21	14.22	14.36
	L ₃	24.17	24.20	24.43
	M ₂	2.653	2.656	2.688
	M ₃	5.123	5.131	5.201
92	L ₂	27.18	27.20	27.43
	L ₃	43.48	43.52	43.88
	M ₂	5.008	5.013	5.060
	M ₃	9.677	9.782	9.894

The difference between the values with $\alpha=2/3$ and with $\alpha=1$ decreases with increasing Z and increases when the initial atomic shell approaches to outer shells. This is because the choice of α more strongly affects on the energy eigenvalues and wave functions of outer-shell electrons. In the case of Cu ($Z=29$), the M₃-shell electrons stay near to the outer-most shell, while the M₃-shell electrons in U ($Z=92$) are screened

from the outer-shell electrons by many intermediate electrons. This is the reason for the Z dependence of the difference.

The largest difference studied in the present work is 3.1% for the M_3 -K transition in copper. It is usual to use the value of α between $2/3$ and 1 for atomic and molecular calculations. If we adopt $\alpha=0.7$, the difference becomes less than 3% for all cases. Therefore we can say that the choice of the statistical exchange parameter is not important for calculations of K x-ray emission rate, when we are interested in the accuracy worse than a few percent.

For lighter elements, the L- and M-shell electrons are outer-shell electrons. On the other hand, for L and M-shell x-ray emission the electron transition from outer shells play an important role. In these cases the effect of choice of α would become more important.

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