

## Analytical Expression of the Hartree-Fock Wave Functions

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A method to fit the atomic wave functions obtained numerically by the Hartree-Fock method to analytical functions has been tested. The fitting function is expressed in terms of Slater-type orbitals (STO's) with integral principal quantum numbers. For the fixed principal quantum number in each STO, both orbital exponent and expansion coefficient have been determined by the use of the nonlinear least-squares method. The obtained wave functions are used to calculate the mean radial distances and the x-ray emission rates in the analytical form. The present results are compared with those obtained using the original numerical wave functions and with those by the Hartree-Fock-Roothaan method.

KEY WORDS : Hartree-Fock wave functions/Slater-type orbitals/Nonlinear least-squares method/

### 1. INTRODUCTION

In order to calculate realistic energy eigenvalues and wave functions of electrons in complex atoms, it is usual to use the self-consistent-field method, such as the Hartree-Fock (HF) method.<sup>1,2)</sup> Froese-Fischer<sup>3)</sup> developed the computer code to calculate atomic structures in the HF method and the Hartree-Fock-Slater (HFS) program was written by Herman and Skillman.<sup>4)</sup> These two computer programs have been frequently used to obtain energy eigenvalues and wave functions of atomic electrons. The atomic wave functions thus obtained are often applied to estimate various physical quantities important in atomic physics, such as oscillator strengths. However, the wave functions in both programs are given numerically at the fixed radial mesh points and it is necessary to carry out numerical derivation or integration as well as interpolation techniques in evaluation of matrix elements.

There have been reported several attempts to obtain atomic wave functions in analytical forms. Roothaan<sup>5)</sup> proposed to expand atomic wave function in terms of a set of analytical basis functions and to solve the HF equation as a matrix eigenvalue problem. This method, called the Hartree-Fock-Roothaan (HFR) method, was originally developed for closed-shell atoms, but later extended to more general open-shell cases.<sup>6)</sup> For atomic structure calculations, it is usual to use Slater-type orbitals (STO's) with integral principal quantum numbers as basis functions. On the

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other hand, in the case of molecular orbital method Gaussian-type orbitals (GTO's) are more frequently used as basis functions for atomic orbitals because of convenience of multi-center integration of wave functions.

Clementi and Roetti<sup>7)</sup> published extensive numerical tables of the HFR wave functions for neutral atoms and ions with atomic numbers  $Z \leq 54$ . A similar table for  $55 \leq Z \leq 92$  has been prepared by McLean and McLean.<sup>8)</sup> For GTO's, Fuzinaga *et al.*<sup>9)</sup> reported a computer code for atomic structure calculations. The relativistic Hartree-Fock-Roothaan (RHFR) method has been developed for closed-shell atoms by Kim<sup>10)</sup> and for open-shell systems by Kagawa.<sup>11)</sup> They employed the STO's with non-integer principal quantum numbers as basis functions. The RHFR wave functions were used for analytical calculations of the momentum distribution of atomic electrons<sup>12)</sup> and the relativistic radiative transition rates.<sup>13)</sup>

The second method to obtain analytical atomic wave functions is to expand atomic wave functions in terms of a finite basis set of square integrable ( $L^2$ ) functions and to diagonalize an atomic Hamiltonian with an appropriate atomic potential. This method has been applied in most cases for hydrogenic potentials with various  $L^2$  functions, such as Laguerre polynomials,<sup>14,15)</sup> Gaussian functions,<sup>14)</sup> Sturmian functions,<sup>16)</sup> and  $B$ -spline functions.<sup>17)</sup> Mukoyama and Lin<sup>18)</sup> used the STO's as basis functions and applied the  $L^2$  expansion method for the case of the HFS potentials. They could reproduce the energy eigenvalues and atomic wave functions calculated in the HFS method. The relativistic extension of this method for hydrogenic potentials has been described in the recent reviews by Drake and Goldman<sup>19)</sup> and by Grant.<sup>20)</sup> Using the STO's, Mukoyama and Lin<sup>21,22)</sup> obtained the solutions of the Dirac equation for atoms in the Dirac-Fock-Slater (DFS) potential and showed that energy eigenvalues and eigenfunctions are good approximation to the numerical solutions. The mean values of  $1/r$ ,  $r$ , and  $r^2$  as well as the x-ray emission probabilities calculated analytically by the  $L^2$  basis functions were in good agreement with those by the numerical DFS wave functions.<sup>22)</sup>

In the present work, we test the third approach to obtain atomic wave functions in analytical forms. This method is based on the technique to fit the numerical functions to the analytical functions by the use of the least-squares method. In the present paper, we use the HF code<sup>3)</sup> to calculate the numerical HF wave functions and employ the STO's similar to those used by Clementi and Roetti<sup>7)</sup> in the HFR method as the fitting functions. The obtained wave functions are used to evaluate the mean values of the power of the radial distance and the x-ray emission rates. These quantities calculated in the present method are compared with those from the numerical HF wave functions and from the HFR wave functions.

## 2. COMPUTATIONAL METHOD

Let  $\phi(r)$  the radial part of the HF wave function obtained numerically by the HF code.<sup>3)</sup> We expand  $\phi(r)$  in terms of a set of basis functions  $\chi(r)$ ,

$$\phi(r) = \sum_{i=1}^N c_i \chi_i(r), \quad (1)$$

where  $r$  is the radial distance,  $N$  is the number of basis functions, and  $c_i$  is the expansion coefficient.

We choose the STO's as basis functions.<sup>7,8)</sup>

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$$\chi_i(r) = N_i r^{n_i-1} \exp(-\zeta_i r). \quad (2)$$

Here  $n_i$  is the principal quantum number and  $\zeta_i$  is the orbital exponent of the STO. The normalization factor  $N_i$  is given by

$$N_i = \frac{(2\zeta_i)^{n_i+1/2}}{[\Gamma(2n_i+1)]^{1/2}}, \quad (3)$$

where  $\Gamma(x)$  is the gamma function.

Choosing appropriate values for  $N$  and  $n_i$  ( $i=1, \dots, N$ ), we determine the most suitable values for  $c_i$  and  $\zeta_i$  by the least-squares method. Since  $\chi_i(r)$  is a nonlinear function with respect to the variable  $\zeta_i$ , we use the nonlinear function minimization method developed by Powell.<sup>23)</sup> Starting from initial estimates of these parameters, the best values are determined by the iteration method.

### 3. RESULTS AND DISCUSSION

All the numerical computations in the present work have been performed on the FACOM M-760/10 computer in the Institute for Chemical Research, Kyoto University.

In Table I, the calculated results of the present method for neutral Li ( $Z=3$ ) atom are compared with the HFR values of Clementi and Roetti.<sup>7)</sup> First, the numerical calculation of the HF wave functions were made for  $(1s)^2(2s)^1$  configuration by the use of the computer program written by Froese Fischer.<sup>3)</sup> The obtained wave functions for the  $1s$  and  $2s$  orbitals were fitted to the STO's using the HFR parameters<sup>7)</sup> as the initial estimates. Since the phase factor of the HF wave functions in the HF code<sup>3)</sup> is different from that of the HFR ones in Ref. 7, the sign of the HF wave function is sometimes different from that of the HFR function. However, in the present work we always choose of the sign of the wave function to be same as that of the HFR tables. It

Table I. Comparison of the parameters between the present method and the HFR method (Ref. 7) for neutral Li atom

Shell	$n_i$	Present		HFR	
		$\zeta_i$	$c_i$	$\zeta_i$	$c_i$
1s	1	2.47673	0.89785	2.47673	0.89786
	1	4.69877	0.11131	4.69873	0.11131
	2	0.40457	-0.00008	0.38350	-0.00008
	2	0.65747	0.00112	0.66055	0.00112
	2	1.07087	-0.00216	1.07000	-0.00216
	2	1.63277	0.00884	1.63200	0.00884
2s	1	2.47663	-0.14628	2.47673	-0.14629
	1	4.69867	-0.01516	4.69873	-0.01516
	2	0.38410	0.00377	0.38350	0.00377
	2	0.66054	0.98052	0.66055	0.98053
	2	1.07017	0.10972	1.07000	0.10971
	2	1.63206	-0.11022	1.63200	-0.11021

is clear that the present results are in good agreement with the values of Clementi and Roetti,<sup>7)</sup> except for the case of the orbital exponents of the  $1s$  orbital.<sup>24)</sup>

Table II shows the comparison of the present results for the  $2p$  and  $3d$  orbitals in the neutral atom of copper ( $Z=29$ ) with the corresponding values of the HFR method.<sup>7)</sup> The estimations of the parameters were performed in the manner similar to the case of Li. It can be seen from the table that both sets of parameters are in good agreement with each other. This fact indicates that the shape of the atomic wave functions in both models is quite similar.

Using the analytical wave functions thus obtained, we attempted to calculate three mean values,  $\langle 1/r \rangle$ ,  $\langle r \rangle$ , and  $\langle r^2 \rangle$ . In the present case, the wave functions are expressed in terms of the STO's and these quantities can be calculated analytically. For this purpose, we used the integration formula:

$$\int_0^{\infty} \exp(-ax)x^n dx = \frac{\Gamma(n+1)}{a^{n+1}}. \quad (4)$$

The typical examples of the calculated results for Cu ( $Z=29$ ), Ag ( $Z=47$ ), and Au ( $Z=79$ ) are shown in Table III and compared with the values obtained directly from the HF wave functions by numerical integration.<sup>3)</sup> In the case of Au, the initial estimates were taken from the table of McLean and McLean.<sup>8)</sup> It is seen that the good agreement is achieved, i.e. the discrepancy is smaller than 1%.

The obtained analytical wave functions were also used to calculate the x-ray emission rates. In the dipole approximation, the x-ray emission rate per second is expressed as<sup>25)</sup>

$$T = 8.0 \times 10^9 \frac{N_i}{3} \frac{\max(l_i, l_f)}{(2l_i + 1)} E_{if}^3 D_{if}^2, \quad (5)$$

where  $N_i$  is the number of electrons in the initial state from which the electron makes a transition,

Table II. Comparison of the parameters between the present method and the HFR method (Ref. 7) for neutral Cu atom.

Shell	$n_i$	Present		HFR	
		$\zeta_i$	$c_i$	$\zeta_i$	$c_i$
$2p$	2	12.53886	0.79137	11.88610	0.84302
	2	20.27416	0.09142	19.58060	0.11714
	3	11.13490	0.13865	10.83980	0.04499
	3	6.98049	0.01994	7.30670	0.03012
	3	4.54172	-0.00343	4.57017	-0.00511
	3	3.07109	0.00128	2.89365	0.00182
$3d$	3	4.95959	0.35235	5.21851	0.29853
	3	13.26012	0.02626	12.96880	0.02649
	3	7.54309	0.21390	7.61139	0.18625
	3	3.01349	0.40485	3.18734	0.42214
	3	1.74572	0.17304	1.66248	0.26291

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 Table III. Comparison of the mean values  $\langle 1/r \rangle$ ,  $\langle r \rangle$ , and  $\langle r^2 \rangle$  between the present method and the HF method (Ref. 3), (a.u.).

Z	Shell	$\langle 1/r \rangle$		$\langle r \rangle$		$\langle r^2 \rangle$	
		Present	HF	Present	HF	Present	HF
29	1s	28.5136	28.5141	0.052881	0.052879	0.003748	0.003748
	2p	6.1572	6.1572	0.207546	0.207546	0.052750	0.052750
	3d	1.4566	1.4566	0.918248	0.918257	1.104507	1.104803
47	2s	10.5975	10.5975	0.140267	0.140266	0.023126	0.023126
	3p	3.6963	3.6963	0.371401	0.371392	0.159868	0.159870
	4d	1.0163	1.0163	1.311885	1.312110	2.070060	2.711139
79	3s	7.1783	7.1784	0.203299	0.203300	0.047103	0.047103
	4p	3.0455	3.0456	0.451394	0.451400	0.231039	0.231041
	5d	0.8756	0.8756	1.487310	1.489527	2.594358	2.609165

 Table IV. Comparison of x-ray emission rates ( $\text{sec}^{-1}$ ) between the HFS, HFR, HF, and the present methods.

Z	Transition	Factor <sup>a)</sup>	HFS <sup>b)</sup>	HFR <sup>c)</sup>	HF <sup>d)</sup>	Present
29	$K-L_{23}$	14	8.7343	8.9875	8.9851	8.9841
	$K-M_{23}$	14	1.0556	1.0460	1.0613	1.0610
	$L_1-M_{23}$	12	6.7721	7.1869	7.2947	7.2950
	$L_{2,3}-M_1$	11	4.2980	4.8942	4.9308	4.9318
47	$K-L_{23}$	15	6.9779	7.0929	7.0930	7.0934
	$K-M_{23}$	15	1.1650	1.1879	1.1866	1.1873
	$K-N_{23}$	14	1.9193	1.7739	1.8071	1.8039
	$L_1-M_{23}$	14	0.9697	1.0136	1.0136	1.0136
	$L_1-N_{23}$	13	1.7201	1.6590	1.6837	1.6833
	$L_{2,3}-M_{4,5}$	14	1.6388	1.7178	1.7169	1.7165
	$M_1-N_{2,3}$	13	5.3506	5.6079	5.6137	5.6156
79	$K-L_{23}$	16	6.1685	6.2245	6.2241	6.2243
	$K-M_{23}$	16	1.2488	1.2643	1.2642	1.2644
	$K-N_{23}$	15	2.9158	2.9216	2.9237	2.9232
	$K-O_{23}$	14	4.9739	4.4312	4.5356	4.5435
	$L_1-M_{23}$	15	1.2488	1.2789	1.2788	1.2789
	$L_1-N_{23}$	14	3.1369	3.1917	3.1998	3.1998
	$L_{2,3}-M_{4,5}$	15	2.1540	2.2094	2.2087	2.2086
	$L_{2,3}-N_{4,5}$	14	3.9764	4.0583	4.0614	4.0618
	$M_1-N_{2,3}$	13	5.3506	5.6079	5.6137	5.6156

<sup>a)</sup>n means  $\times 10^n$ .

<sup>b)</sup>Hartree-Fock-Slater method (Ref. 26).

<sup>c)</sup>Hartree-Fock-Roothaan method (Ref. 7).

<sup>d)</sup>Hartree-Fock method (Ref. 3).

$E_{if}$  is the x-ray transition energy in Rydberg,  $D_{if}$  is the dipole matrix element, and  $l_i$  and  $l_f$  are the orbital angular momenta in the initial and final states, respectively. The dipole matrix element is given by

$$D_{if} = \langle \phi_f | r | \phi_i \rangle, \quad (6)$$

where  $\phi_i$  and  $\phi_f$  are the initial- and final-state wave functions of the electron. Inserting Eq. (1) into Eq. (6), the dipole matrix element and then the x-ray emission rate can be expressed in the analytical form by the use of Eq. (4).

The x-ray emission rates calculated in this manner are compared with those from the HFS, the HFR, and the HF wave functions. The HFS values were taken from the table prepared by Manson and Kennedy<sup>26)</sup> and the HFR values were calculated in the manner similar to the present work by the use of the tabulated parameters by Clementi and Roetti<sup>7)</sup> and by McLean and McLean.<sup>8)</sup> The HF values were obtained by numerical integration using the HF wave functions.<sup>3)</sup> In Table IV, the comparison is shown for several strong x-ray components in Cu, Ag, and Au. The present results are in good agreement with the values obtained by the HF wave functions numerically. These two values agree also with the HFR values. The HFS values are in agreement with other three values for inner-shell transitions, but there is discrepancy up to several percents in the case of outer-shell transitions. This difference can be ascribed to the Slater approximation for the exchange potential used in the HFS method.

#### 4. CONCLUSION

The analytical form of the atomic HF wave functions has been obtained by the use of the nonlinear least-squares method. The numerical HF wave functions were fitted to the sum of the STO's with integral principal quantum numbers, and the expansion coefficients and orbital exponents were determined by the Powell's nonlinear function minimization method. The obtained wave functions were used to calculate the mean values of  $\langle 1/r \rangle$ ,  $\langle r \rangle$ , and  $\langle r^2 \rangle$ , and the x-ray emission rates. The results in the present method are in good agreement with the values obtained numerically from the original HF wave functions. This fact indicates that the present analytical wave functions are good approximation to the numerical HF wave functions.

The advantage of the use of the analytical wave functions is the fact that all the calculations described above can be performed analytically. It is also possible to obtain other quantities, such as the momentum wave functions, in the analytical form.

In comparison with other methods for analytical wave functions, the great advantage of the present method consists in its simplicity. There is no need to calculate the wave functions self-consistently, as in the HFR method, and it is unnecessary to solve a generalized eigenvalue problem, as in the case of the  $L^2$  expansion method. This fact means that the number of basis functions can be chosen to be larger than in other methods and the calculations are stable when appropriate initial estimates of the parameters are used.

In the present work, we used the STO's as fitting functions and fitted them to the HF wave functions. However, the present method can be used in more general cases. It is possible to choose any kinds of analytical functions as basis functions and to fit them to any numerical atomic wave functions. The type of the basis function and the atomic wave function should be determined

by considering the problem to be solved and the quantity to be calculated. For example, in the case of molecular orbital calculations the GTO's would be more suitable basis functions. Furthermore, it is possible to extend the present method to the relativistic case and to obtain the analytical wave functions corresponding to the Dirac-Fock or DFS wave functions.

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