L^2 Approximation of Atomic Continuum Wave Functions

Takeshi MUKOYAMA* and Gábor HOCK†

The approximation of atomic continuum wave function by an L^2 basis set has been studied using the Slater-type orbitals. The numerical continuum wave function is fitted to analytical basis functions with the least-squares method. It is shown that for low-energy electrons and for small radial distances the present method can give good approximation to numerical wave functions in the Hartree-Fock-Slater field.

KEY WORDS: Continuum wave function/ Hartree-Fock-Slater method/ Analytical expression

1. INTRODUCTION

For many-electron systems, realistic energy eigenvalues and wave functions are generally obtained as numerical solutions of the Schrödinger equation with the self-consistent-field (SCF) potential.[1,2] The Hartree-Fock (HF) and Hartree-Fock-Slater (HFS) methods are often used for this purpose. In this case, the wave functions are given usually in numerical forms. However, in order to evaluate matrix elements for atomic transitions, such as radiative rates and inner-shell ionization cross sections, it is more convenient to use analytical wave functions.

For bound states, there have been reported several attempts to calculate analytical wave functions. The most frequently used method is the Hartree-Fock-Roothaan (HFR) method.[3] The atomic wave functions are expanded in terms of a set of basis functions and the HF equation is solved as a matrix eigenvalue problem.

In atomic collisions, the finite-basis-set expansion method has often been adopted. The atomic wave functions are expanded in terms of a finite basis set of square-integrable (L^2) functions and an atomic Hamiltonian with an appropriate atomic potential is diagonalized to obtain energy eigenvalues and wave functions.[4] Since the atomic potential is unchanged in this method, the iteration procedure is unnecessary and the computation time is significantly reduced in comparison with the HFR method. Recently we have developed an alternative approach to obtain analytical wave functions.[5] This method consists in fitting analytical functions to the SCF wave functions computed numerically.

On the other hand, for continuum states the number of methods which have been used to express wave functions in analytical forms is scarce. The finite-bases-set method described above, sometimes called the L^2 *discretization method* or *the pseudostate method*, has been applied to

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* 向山　毅 : Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611 Japan.
† Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, Hungary.

many problems in atomic and molecular ionization processes.[4,6]   When the number of the basis set is finite, in addition to the bound sates which have negative energies we obtain the states with positive discrete energy eigenvalues, called *pseudostates*.

The eigenfunctions corresponding to these pseudostates should contain some information about the continuum states with the same kinetic energies and can be used as approximate wave functions to continuum wave functions, though the normalization conditions for two wave functions are different.   As basis functions, various L^2 functions have been used, such as Laguerre polynomials,[7,8] Slater-type orbitals (STO's),[4] Gaussian-type orbitals,[9] Sturmian functions,[10] B-spline functions,[11] and Lobatto functions.[12]

The pseudostate method is a very powerful technique to express continuum states in analytical forms and has been successfully applied for many problems.   However, it is difficult to obtain the wave function corresponding to a definite kinetic energy, because the energy eigenvelues of the pseudostates are determined by diagonalization of the atomic Hamiltonian. In order to evaluate the transition matrix element for a definite kinetic energy using pseudostates, special numerical techniques, such as the Stieltjes imaging,[6] should be used.   Furthermore, since the pseudostates are obtained together with the bound states the size of basis set becomes larger.   This fact is sometimes trouble when a dense discrete spectrum with positive energies is necessary.

In the present work, we present a method to calculate an analytical continuum wave function with an arbitrary kinetic energy.   The present method is an extension of our previous works for the bound states[5,13] to the continuum case.   First the continuum wave function is computed numerically by solving the single-particle Schrödinger equation for an appropriate atomic potential.   The phase shift and the normalization constant are evaluated in the conventional way for the continuum wave function.   Then the numerical wave function is fitted to analytical L^2 functions with the least-squares method.   Here we demonstrate the validity of the method for the examples of neutral atoms with the HFS potential using the STO's as basis functions.

2. COMPUTATIONAL METHOD

The single-particle wave function for the continuum state is given as the solution to the radial Schrödinger equation:

$$\frac{d^2 P_{kl}(r)}{dr^2} + \left[k^2 - 2V(r) - \frac{l(l+1)}{r^2}\right] P_{kl}(r) = 0. \tag{1}$$

Here $V(r)$ is the atomic potential, l is the orbital angular momentum quantum number, and k is the wave number of the free electron, that is $k = (2E)^{1/2}$, where E is the kinetic energy of the electron.   Throughout the present work atomic units $(\hbar = m = e = 1)$ are used.

In neutral atoms, the atomic potential vanishes faster than the Coulomb field and $V(r) \to 0$ for $r \to \infty$.   For sufficiently large r values, Eq. (1) reduces to

$$\frac{d^2 P_{kl}(r)}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right] P_{kl}(r) = 0. \tag{2}$$

In this asymptotic region, the continuum wave functions are of the form[14]

$$P_{kl}(r) = \sqrt{\frac{2}{\pi k}} kr \left[\cos \delta_l j_l(kr) - \sin \delta_l n_l(kr)\right], \tag{3}$$

where δ_l is the phase shift, and $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions

with order l, respectively.

The solution of Eq. (1) should joint smoothly to Eq. (3) at the practical infinity $r=r_\infty$. From this condition, the phase shift can be determined as

$$\tan \delta_l = \frac{kj'_l(kr_\infty)-\beta j_l(kr_\infty)}{kn'_l(kr_\infty)-\beta n_l(kr_\infty)}, \tag{4}$$

where the primed quantity means the derivative with respect to r and

$$\beta = \frac{P'_{kl}(r_\infty)}{P_{kl}(r_\infty)} - \frac{1}{r_\infty}. \tag{5}$$

The normalization constant is decided at $r=r_\infty$ and the normalized continuum wave function is obtained.

In order to express $P_{kl}(r)$ obtained above in analytical forms, we expand it in terms of basis functions $\chi(r)$

$$P_{kl}(r) = \sum_{n=1}^{N} \xi_i \chi_i(r), \tag{6}$$

where ξ_i is the expansion coefficient and N is the number of basis functions. In the present work, we use the STO's as basis functions:[5,13]

$$\chi_i(r) = N_i r^{n_i} \exp(-\zeta_i r). \tag{7}$$

Here N_i is the normalization constant for the STO, n_i is an integer, and ζ_i is the orbital exponent.

For the fixed values of N and n_i, the most suitable values for ξ_i and ζ_i are determined by fitting Eq. (6) to the numerical continuum wave function $P_{kl}(r)$ with the least-squares method using the nonlinear function minimization procedure.[15]

3. RESULTS AND DISCUSSION

The numerical calculations in the present work have been performed on the FACOM M-1600/6 computer in the Institute for Chemical Research, Kyoto University.

The atomic potentials were calculated in the HFS method in the manner similar to the Herman-Skillman program,[16] but the Latter tail correction[17] is omitted so as to fulfill the boundary condition described above. Using this atomic potential, the continuum wave function with a certain kinetic energy is obtained by solving the Shrödinger equation numerically.

The numerical wave function was fitted to the sum of the STO's in Eq. (6). The initial estimates for fitting were taken from the table of Clementi and Roetti[18] for the HFR wave functions. For $l=0$, we used the parameters for the $2s$ electron as the initial estimates, because the ξ_i values for the $1s$ electron are almost zero except for one. The values of N and n_i were fixed in their original values and the parameters ξ_i and ζ_i were determined using the nonlinear least-squares method between $r=0$ and $10/Z$, where Z is the atomic number.

Test calculations were made for the case of Ne atom. Table I lists the ξ_i and ζ_i values for $2s$ electron, taken from the Clementi-Roetti table and used as the initial estimates, and the fitted results for the electron with the energy of 1 a.u. and 10 a.u. and with the orbital angular momentum of $l=0$. The obtained analytical continuum wave function for $E=1$ and $l=0$ is shown in Fig. 1 and compared with the numerical continuum wave function. The relative difference between two wave functions in % is plotted in Fig. 2 against the radial distance r. It can be seen from the figures that agreement between both wave functions is quite good. The

Table I. Comparison of parameters of STO's of Ne for the continuum electron with $E=1$ and 10 and $l=0$ with those for the $2s$ electron.

n_i	ξ_i			ζ_i		
	$2s$[a]	$E=1$	$E=10$	$2s$[a]	$E=1$	$E=10$
1	−0.231	−0.779	−0.525	9.485	8.331	3.069
1	−0.006	−0.501	−1.481	15.566	9.205	3.623
2	0.186	0.807	5.969	1.962	3.430	5.485
2	0.669	−12.602	−8.910	2.864	1.001	−0.003
2	0.309	0.415	−2.830	4.825	3.356	2.335
2	−0.139	−2.205	−2.061	7.792	4.476	7.254

[a] Clementi and Roetti, Ref. 18.
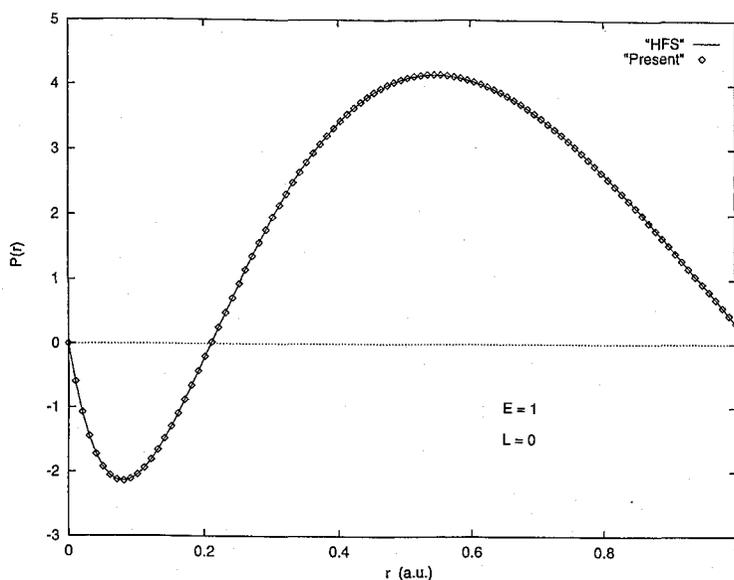
Fig. 1. Comparison of the analytical wave function for Ne with $E=1$ and $l=0$ with the numerical one. The solid line represents the numerical wave function in the HFS field and ◇ symbol indicates the present result.

deviation is less than 1% in the region of r in the figures. The large deviation is found at the points near to the node of the continuum wave function, where the absolute values are small and slight difference in wave functions gives rise to large relative deviation.

Figure 3 shows the conparison of the wave functions of Ne $l=0$ state with $E=10$. In this case, the analytical wave function is also a good approximation to the numerical continuum wave function, but the relative deviation from the latter is larger, less than 15%, in comparison with the case of $E=1$. This suggests that for high-energy electrons larger basis sets involving large n_i values are needed to represent quick oscillation. For the case of $l=1$, the similar comparison is made for $E=1$ in Fig. 4. In this case, the number of basis functions is only four, but we can still obtain good agreement with the numerical wave functions.

The present results indicate that for low-energy region and for small radial distance the L^2 expansion method with STO's can give good approximation to the continuum wave function.
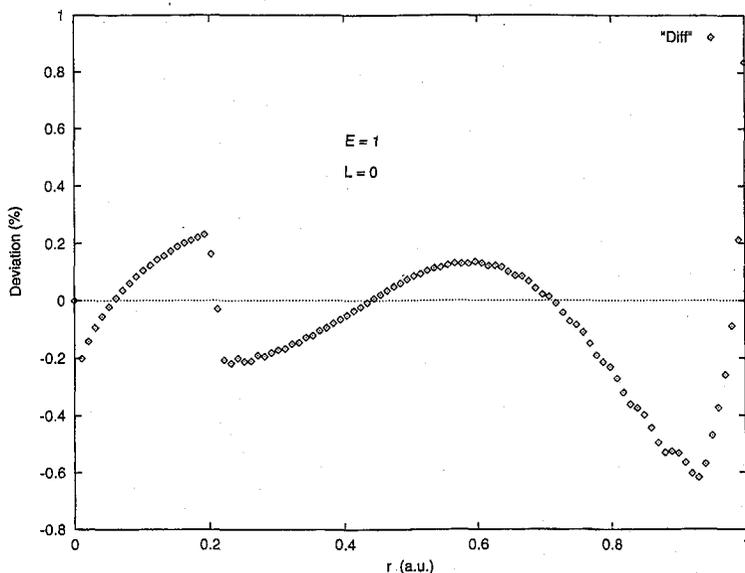
Fig. 2. Relative deviation for Ne with $E=1$ and $l=0$ from the numerical one.
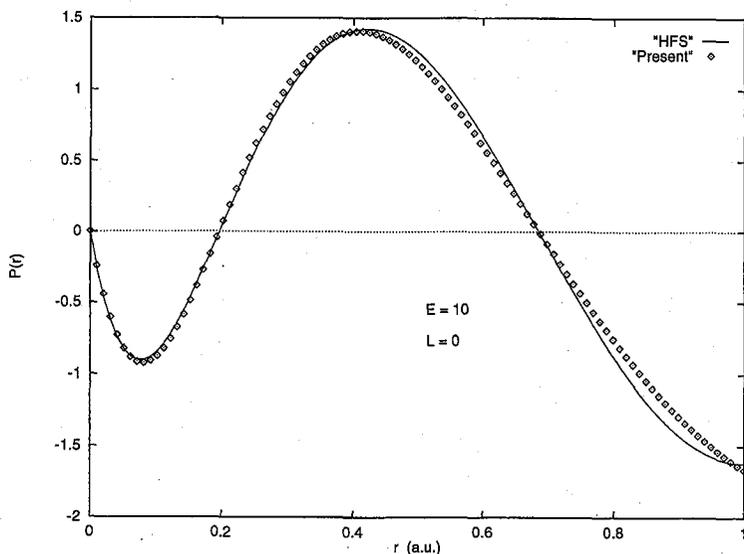
Fig. 3. Same as Fig. 1, but for $E=10$ and $l=0$.

4. CONCLUSION

We presented the method to express the atomic continuum wave function in the form of analytical functions.   The numerical wave functions for the continuum states were fitted to the sum of the STO's, as in the case for bound states.   The expansion coefficients and the orbital exponents in STO's were determined by the nonlinear function minimization method of Powell.[15]   The obtained wave functions are good approximation to the numerical continuum wave functions for the energy range and the region of radial distance considered, though the number of basis functions is small, $N=6$ for $l=0$ and $N=4$ for $l=1$.   This fact suggests that for
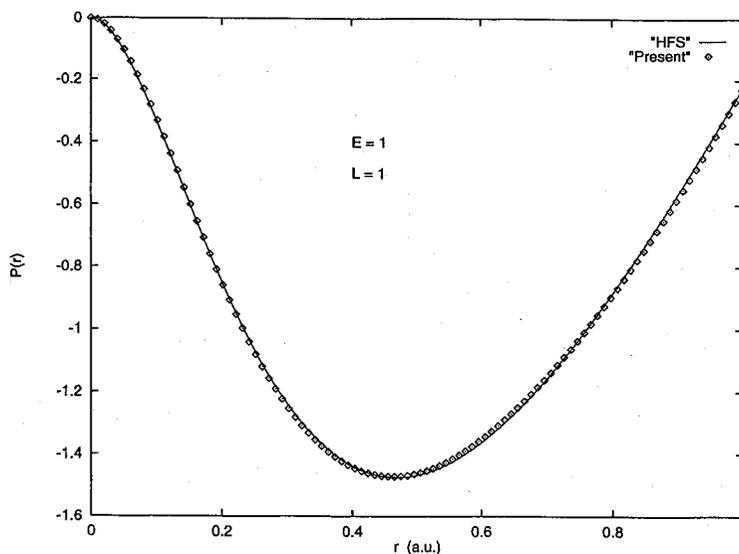
Fig. 4. Same as Fig. 1, but for $E=1$ and $l=1$.

inner-shell electron ejection in low-energy region the present method is useful to calculate the transition matrix elements analytically, because dominant contributions come from the small-r region.

However, our results in the pseudostate method[4] indicate that for higher energies and for larger radial distances the STO's cannot reproduce the oscillatory behavior of the exact continuum wave functions and are not good basis functions. In such cases, we must use different basis functions and probably different techniques.

In the present work, we used the STO's as basis functions and the atomic potential was obtained for neutral atoms with the HFS method. However, the principle of the present method is more general. One can use any kinds of basis functions and arbitrary potentials, not only for neutral atoms but also for ions. Such calculations are made simply by changing the boundary conditions and asymptotic forms of wave functions.

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