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Abstract. —— The solutions of the matrix representation of the Dirac equation for atoms in the Dirac-Fock-Slater potential are obtained by the finite-basis-set expansion method. Slater-type orbitals are used as basis functions. The energy eigenvalues are in good agreement with those obtained from the numerical solution of the Dirac equation except for a spurious root for $\kappa > 0$. Despite this spurious root, the present method is found to give good approximate atomic energy eigenvalues and wave functions.

The finite-basis-set expansion method is well known to be very useful to calculate approximate energy eigenvalues and wave functions for atoms and molecules in the nonrelativistic case. However, the extension of this method to the relativistic case is not trivial because the Dirac Hamiltonian is not bounded from below. Recently, Drake and Goldman [1] demonstrated that stable variational solutions to the Dirac equation for a pure Coulomb field can be obtained by the basis-set expansion method. They also found that a spurious root always appears for $\kappa > 0$, where κ is the Dirac quantum number.

In the present work, we apply the finite-basis-set expansion method to the solutions of Dirac equations for more realistic atomic potential, i.e. the Dirac-Fock-Slater (DFS) potential. We expand the large and small components of the radial wave function in terms of Slater-type orbitals (STO's) with nonintegral principal qunatum number:

$$f(r) = (2\zeta)^{n'+1/2} [\Gamma(2n'+1)]^{-1/2} r^{n'} \exp(-\zeta r),$$

with

$$n' = n + (\kappa^2 - \alpha^2 Z^2)^{1/2} - |\kappa|, \qquad n = 1, 2, \cdots\cdots$$

where ζ is the orbital exponent, $\Gamma(x)$ is the gamma function, Z is the atomic number and α is the fine structure constant. Using this basis set with appropriate choice of n and ζ, the Dirac Hamiltonian for a DFS potential is diagonalized to obtain the energy eigenvalues and atomic wave functions.

The results for $\kappa = -1$ in gold ($Z = 79$) are shown in Table 1. The atomic potential is generated by a computer program equivalent to the DFS program of Liberman, Cromer and Waber [2]. The negative energy eigenvalues in the present work are in good agreement with those obtained from the numerical solutions of the Dirac equation with the same DFS potential. In order to demonstrate the relativistic effects,

Table 1. Comparison of relativistic and nonrelativistic energy eigenvalues for $\kappa = -1$ in gold (a.u.).

		Relativistic		Nonrelativistic
n	ζ	DFS[a]	HFS[b]	HFS[c]
1	77.6	-2975.0	-2998.0	-2695.2
2	77.6	-526.85	-536.70	-451.89
3	77.6	-124.99	-128.43	-106.36
3	48.5	-27.477	-28.620	-22.766
3	30.3	-4.239	-4.546	-3.345
3	18.9	0.279	0.170	0.569
3	11.8	13.849	13.37	16.534
3	7.4	165.26	161.06	196.50
3	4.6	1229.6	1215.8	1542.4
3	2.9	7003.1	7030.8	12460.0

a) Dirac equation with DFS potential.
b) Dirac equation with HFS potential.
c) Schrödinger equation with HFS potential.

Table 2. Energy eigenvalues of the states with $\kappa = 1$ and -2 in gold (a.u.) and the parameters used for the basis-set expansion. The value in the parenthesis indicates the spurious root.

n	ζ	$\kappa = 1$	$\kappa = -2$
2	36.45	-505.76	-438.09
2	16.70	-115.50	-100.46
3	36.45	-23.370	-19.747
3	16.70	-2.8893	-2.2577
3	14.00	-0.1195	-0.08967
4	9.25	0.3684	0.4899
4	6.13	3.550	4.158
5	4.45	23.935	25.364
5	2.50	136.07	137.27
5	1.45	1117.4	829.68
1	77.60	(-3057.1)	

the relativistic and nonrelativistic calculations with the nonrelativistic Hartree-Fock-Slater (HFS) potential [3] are also made and listed in the table. In the case of the nonrelativistic calculations, we used the STO's with integer principal quantum number in the table and the obtained results agree very well with the numerical results [3]. It is clear that the use of the Dirac equation increases the energy eigenvalues substantially and the relativistic effect in the atomic potential is not so large.

Table 2 shows the results for $\kappa = 1$ and -2 in gold. The same basis set was used for both cases, except that an additional STO corresponding to the lowest $\kappa = -1$ state is added to the case of $\kappa = 1$, to account for additional node in the small component. The negative energy eigenvalues are in agreement with the numerical solutions of the Dirac equation. It can be seen that there is a spurious root indicated by the parenthesis, which is degenerate with the root for $\kappa = -1$. Despite of this spurious root, we found

that the analytical wave functions for the bound states with $\kappa = 1$ can well reproduce the behavior of those obtained by the numerical solutions.

We have also calculated the K-x-ray emission rates for copper ($Z = 29$), silver ($Z = 47$) and gold ($Z = 79$) by the use of the analytical atomic wave functions in the present work. The K-x-ray transition probabilities from the L and M shells thus obtained are in good agreement with those calculated with the numerical DFS wave functions [4].

In conclusion, we have shown that the finite-basis-set expansion method can be applied to the Dirac equation for atoms. Although there exists a spurious root for $\kappa > 0$, this root can easily be identified and causes no trouble to use the present method for atomic and molecular calculations.

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