

## Finite-basis-set approach to the Dirac equation for atoms in a Dirac-Fock-Slater potential

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A finite set of Slater-type orbitals is used as a basis to solve the Dirac equation for atoms in a Dirac-Fock-Slater potential. The energy eigenvalues thus obtained are in good agreement with the results from the numerical solution of the Dirac equation except that a spurious root always occurs for  $\kappa > 0$ . It is shown that despite this spurious root the method still gives good approximate atomic energy eigenvalues and wave functions. This implies that the finite-basis-set expansion method can be applied to relativistic atomic structure and atomic collision calculations.

### I. INTRODUCTION

It is well known that approximate energy eigenvalues and wave functions of atoms and molecules in a nonrelativistic formulation can be conveniently calculated as expansions in a finite basis set. For example, many two-center matrix elements are more easily evaluated in terms of Slater or Gaussian orbitals than in terms of numerical wave functions. Recently it has been demonstrated<sup>1-5</sup> that inner-shell ionization cross sections can be calculated with improved approximations if pseudostates, i.e., discretized states with positive energies, are used to approximate the final continuum wave functions.

In the study of inner-shell ionizations of heavy atoms and the structure of molecules consisting of heavy atoms, it is essential to take into account relativistic effects of the inner electrons. In order to go beyond the simple first-order Born approximation (or equivalently, the semiclassical approximation), it is computationally more convenient to be able to represent both the initial and final wave functions in Slater-type basis-set expansion. Similarly, in constructing molecular orbitals for heavy atomic systems, it is desirable to expand the molecular orbitals in terms of analytical atomic orbitals on each center. This is particularly important if the nonadiabatic coupling terms involving the derivatives of molecular orbitals are to be evaluated.

The finite-basis-set expansion method has been applied to the solution of Dirac-Hartree-Fock equations for closed-shell atoms<sup>6</sup> and for open-shell atoms.<sup>7</sup> However, the method is not variationally stable since the Dirac Hamiltonian is not bound from below. To avoid the variational collapse some projection techniques have been proposed.<sup>8-10</sup> This, unfortunately, introduces additional complications to the Dirac Hamiltonian. In a recent paper Drake and Goldman<sup>11</sup> demonstrated that stable variational solutions of the Dirac equation for a pure Coulomb potential can be obtained in a finite-basis-set expansion method. When the number of Slater-type basis functions is  $N$ , the  $2N$  total energy eigenvalues split into  $N$  positive and  $N$  negative values. All the negative eigenvalues lie below  $E = -c^2$  ( $m_e = 1$  and  $c$  is the speed of light), and all the positive eigenvalues behave as if the Dirac Hamil-

tonian were a positive definite operator. However, they found that a spurious root for positive energies always exists for  $\kappa > 0$ . This spurious root is degenerate with the lowest state of the corresponding  $-\kappa$ . Methods have been proposed to remove this spurious root by additional constraints<sup>12-15</sup> and criteria have also been given<sup>16,17</sup> to distinguish acceptable solutions from the spurious ones.

The works quoted above have been demonstrated for the simple pure or modified Coulomb fields, or the more complicated Dirac-Hartree-Fock equations. In this paper we report the application of the finite-basis-set expansion method to the solutions of Dirac equations in a Dirac-Fock-Slater (DFS) potential. Our interest is in the use of relativistic pseudostate wave functions for the calculation of inner-shell ionization cross sections. In this paper we confine ourselves to bound states only. The calculated energies and wave functions are compared with those obtained from the numerical DFS calculations to establish the validity of the method.

### II. METHOD

Our method is essentially the same as that employed by Drake and Goldman.<sup>11</sup> The Dirac equation for an electron in a potential  $V(r)$  is

$$H\psi = E\psi, \quad (1)$$

where  $H$  is

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + c^2\beta' + V(r), \quad (2)$$

$\mathbf{p}$  is the momentum,  $\boldsymbol{\alpha}$  is a  $4 \times 4$  Dirac matrix, and  $\beta'$  is

$$\beta' = \begin{pmatrix} 0 & 0 \\ 0 & -2\mathbf{1} \end{pmatrix}, \quad (3)$$

where  $\mathbf{1}$  is a  $2 \times 2$  unit matrix. In (2), the zero of the energy scale is shifted to the electron's rest-mass energy and the energy eigenvalue thus corresponds to the binding energy. Atomic units are used throughout this work.

The solution of (1) is expressed in the form

$$\psi_{n\kappa m} = \begin{pmatrix} P_{n\kappa}(r)/r & \chi_{\kappa}^m \\ iQ_{n\kappa}(r)/r & \chi_{-\kappa}^m \end{pmatrix}, \quad (4)$$

where  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  are the large and small components of the radial wave function, respectively,  $\chi_{\kappa}^m$  is the spin-angular-momentum wave function, and  $n$  is the principal quantum number.

Following Drake and Goldman we expand the radial wave function in terms of Slater-type orbitals (STO's) with noninteger principal quantum number,

$$f_{\kappa p}(r) = (2\xi_{\kappa p})^{n'_{\kappa p} + 1/2} [\Gamma(2n'_{\kappa p} + 1)]^{-1/2} r^{n'_{\kappa p}} \times \exp(-\xi_{\kappa p} r), \quad (5)$$

with

$$n'_{\kappa p} = n_{\kappa p} + (\kappa^2 - Z^2 \alpha^2)^{1/2}, \quad n_{\kappa p} = 0, 1, \dots \quad (6)$$

where  $\xi_{\kappa p}$  is the orbital exponent,  $\Gamma(x)$  is the gamma function,  $Z$  is the atomic number, and  $\alpha$  is the fine-structure constant. Drake and Goldman used a constant value for  $\xi_{\kappa p}$ , but we choose different values for different  $\kappa$  and  $p$ . Using the basis set defined by (5) with an appropriate choice of  $n_{\kappa p}$  and  $\xi_{\kappa p}$ , the Dirac Hamiltonian (2) with a DFS potential is diagonalized to obtain energy eigenvalues and wave functions. Note that the same STO basis set is used for both the large and small components.

### III. RESULTS AND DISCUSSIONS

Calculations have been carried out for  $\kappa = -1, 1, -2$  for  $Z = 29, 47$ , and  $79$ . The atomic potential for each atom is generated by a program equivalent to that of Liberman, Cromer, and Waber.<sup>18</sup> The STO's are chosen similar to those used in the nonrelativistic theory. Thus, for example, the basis set used for  $\kappa = 1$  and  $\kappa = -2$  are identical. To account for the additional node in the small component for states with  $\kappa > 0$ , it is necessary to add an additional STO corresponding to the lowest state for  $-\kappa$ . For example, the lowest  $\kappa = -1$  STO is added to the  $\kappa = 1$  basis set.

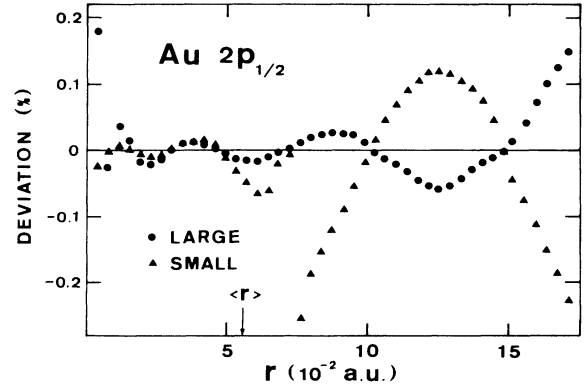


FIG. 1. Relative deviation (%) of the gold  $2p_{1/2}$ -shell wave functions obtained by the basis-set expansion method from the numerical DFS wave functions. The solid circles represent the deviation for the large component and the solid triangles indicate that for the small component. The mean radial distance is shown by an arrow.

When the basis size is  $N$ , the lowest  $N$  eigenvalues are always less than  $-2c^2$  in the present energy scale. They correspond to negative-energy states. We exclude these states from further discussion. In Table I we show the basis set used and the resulting energy eigenvalues for  $Z = 79$ . We notice that the results from the diagonalization are in good agreement with those from the numerical solution of the Dirac equation with the same DFS potential which are given in parenthesis. We also note that in every case the bound-state energies calculated from the finite-basis-set expansion method are slightly higher than the numerical results. If we view the numerical results as exact for the given DFS potential, this result appears to show that the finite-basis-set method also satisfies the variational principle as in the nonrelativistic case. For

TABLE I. Principal quantum number  $n$  and orbital exponent  $\zeta$  for the Slater-type basis functions, and the energy eigenvalues  $E$  obtained by diagonalizing the Dirac Hamiltonian with the DFS potential for gold. The values in the parenthesis are the eigenvalues obtained by the numerical DFS calculation. The spurious root is indicated by an underline.

$\kappa = -1$			$\kappa = 1$			$\kappa = -2$	
$n$	$\zeta$	$E$ (a.u.)	$n$	$\zeta$	$E$ (a.u.)	$E$ (a.u.)	$E$ (a.u.)
1	77.6	-2975.0 (-2975.4)	2	36.45	-505.78 (-506.30)	-438.09 (-438.11)	
2	77.6	-526.85 (-526.91)	2	16.70	-115.50 (-115.58)	-100.46 (-100.46)	
3	77.6	-124.99 (-125.03)	3	36.45	-23.370 (-23.399)	-19.747 (-19.744)	
3	48.5	-27.477 (-27.485)	3	16.70	-2.8893 (-2.8943)	-2.2577 (-2.2567)	
3	30.3	-4.2393 (-4.2434)	3	14.00	-0.1195	-0.08967	
3	18.9	0.2786	4	9.25	0.3684	0.4899	
3	11.8	13.849	4	6.13	3.550	4.158	
3	7.4	165.26	5	4.45	23.935	25.364	
3	4.6	1229.6	5	2.50	136.07	137.27	
3	2.9	7003.0	5	1.45	1117.4	829.68	
			1	77.60	<u>-3057.1</u>		

TABLE II. Comparison of the mean values of  $1/r$ ,  $r$ , and  $r^2$  for various shells in Ag obtained by the basis-set expansion method with those by the numerical DFS calculation.

Shell	$\langle r^{-1} \rangle$		$\langle r \rangle$		$\langle r^2 \rangle$	
	DFS <sup>a</sup>	BS <sup>b</sup>	DFS	BS	DFS	BS
1s	49.51	49.51	3.105[−2] <sup>c</sup>	3.105[−2]	1.303[−3]	1.303[−3]
2s	11.44	11.44	1.340[−1]	1.340[−1]	2.122[−2]	2.122[−2]
2p <sub>1/2</sub>	11.43	11.43	1.134[−1]	1.134[−1]	1.581[−2]	1.581[−2]
2p <sub>3/2</sub>	10.74	10.74	1.185[−1]	1.185[−1]	1.712[−2]	1.712[−2]
3s	4.020	4.020	3.653[−1]	3.653[−1]	1.528[−1]	1.528[−1]
3p <sub>1/2</sub>	3.933	3.933	3.562[−1]	3.552[−1]	1.475[−1]	1.463[−1]
3p <sub>3/2</sub>	3.763	3.769	3.670[−1]	3.658[−1]	1.564[−1]	1.549[−1]
4s	1.543	1.542	9.001[−1]	9.006[−1]	9.185[−1]	9.191[−1]

<sup>a</sup>Numerical DFS calculation.

<sup>b</sup>Basis-set expansion.

<sup>c</sup>3.105[−2] means  $3.105 \times 10^{-2}$ .

$\kappa=1$  we note that there is a spurious root which is indicated by an underline. While for a Coulomb potential, this spurious root is degenerate with the root for  $\kappa=-1$ , in the DFS potential it is slightly lower. If we exclude this root, the energy spectra of  $\kappa=1$  are still well behaved. In the case of a Coulomb potential, the origin of the spurious roots and methods of eliminating these roots have been discussed by Goldman.<sup>13</sup>

We have compared the wave functions obtained from the finite-basis-set expansion method with the numerical results. The agreement for both the large and small components is good. One may wonder how the spurious root would affect the other wave functions. In Fig. 1 we show the  $2p_{1/2}$  radial wave function for  $Z=79$ . The relative difference  $(R_{BS}-R_{DFS})/R_{DFS}$  is plotted as a function of  $r$ , where  $R_{BS}(r)$  and  $R_{DFS}(r)$  are either the large or small component of the wave function from the basis set and

from the numerical solutions, respectively. The location of the mean radial distance is indicated by an arrow. From this figure we note that the error is very small everywhere except in the region where the wave function is small. This occurs for both the large and small components at large  $r$  and for the small component near  $r=0.075$  a.u. where the function has a node. This result demonstrates that the basis-set expansion method can reproduce numerical DFS wave functions even in the presence of a spurious root.

To illustrate the quality of the wave functions obtained by the basis-expansion method, we show the expectation values of  $1/r$ ,  $r$ , and  $r^2$  for various shells of silver ( $Z=47$ ), and compare it in Table II with the results obtained from the numerical DFS wave functions. The agreement is again very good. The exponents in the STO's for Ag were obtained from those for Au by a scal-

TABLE III. Comparison of  $K$  x-ray transition rates (eV/ $\hbar$ ). 3.829[−7] means  $3.829 \times 10^{-7}$ .

Z		RHFR <sup>a</sup>	DFS <sup>b</sup>	Present
29	KL <sub>1</sub>	3.829[−7] <sup>c</sup>	3.929[−7]	3.922[−7]
	KL <sub>2</sub>	0.1885	0.1942	0.1948
	KL <sub>3</sub>	0.3656	0.3788	0.3787
	KM <sub>1</sub>	7.166[−8]	7.637[−8]	7.650[−8]
	KM <sub>2</sub>	0.02199	0.02355	0.02361
	KM <sub>3</sub>	0.04273	0.04605	0.04607
47	KL <sub>1</sub>	6.476[−5]	6.559[−5]	6.559[−5]
	KL <sub>2</sub>	1.559	1.571	1.571
	KL <sub>3</sub>	2.898	2.962	2.962
	KM <sub>1</sub>	1.669[−5]	1.695[−5]	1.693[−5]
	KM <sub>2</sub>	0.2532	0.2583	0.2587
	KM <sub>3</sub>	0.4920	0.5018	0.5028
79	KL <sub>1</sub>	0.01799	0.01812	0.01810
	KL <sub>2</sub>	14.15	14.36	14.35
	KL <sub>3</sub>	23.91	24.43	24.43
	KM <sub>1</sub>	5.558[−3]	5.657[−3]	5.640[−3]
	KM <sub>2</sub>	2.645	2.688	2.687
	KM <sub>3</sub>	5.074	5.201	5.199

<sup>a</sup>RHFR method (Ref. 20).

<sup>b</sup>Numerical DFS method.

<sup>c</sup>Basis-set expansion method.

ing proportional to the atomic  $Z$  number. No optimization was attempted.

Using the wave functions obtained by the present method, the  $K$  x-ray transition probabilities were calculated for copper, silver, and gold. The calculations are based on the expression derived by Scofield.<sup>19</sup> The basis set for Cu was taken from Kagawa.<sup>7</sup> In Table III we compare the transition rates from the present calculation with those obtained by numerical DFS wave functions and with the values calculated by the RHFR method.<sup>20</sup> The present results are in good agreement with DFS values.

#### IV. CONCLUSION

The finite-basis-set expansion method using STO's with noninteger principal quantum numbers has been applied to the Dirac equation with DFS potentials for atoms. With a small basis set, the energy eigenvalues and wave functions obtained are very close to those from the nu-

merical solution of the Dirac equation using the same potential. For  $\kappa > 0$  we note that there is always a spurious root corresponding to the smallest positive-energy eigenvalue. This root is easily identified and it poses no practical limitation to the application of the basis-set expansion method to relativistic atomic and molecular problems. Using pseudostates generated from the basis-set expansion method we are in the process of calculating inner-shell ionization cross sections in ion-atom collisions for heavy atoms.

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<sup>1</sup>A. L. Ford, E. Fitchard, and J. F. Reading, *Phys. Rev. A* **16**, 973 (1983).

<sup>2</sup>R. Shakeshaft, *Phys. Rev. A* **18**, 1930 (1978).

<sup>3</sup>W. Fritsch and C. D. Lin, *Phys. Rev. A* **27**, 3361 (1983).

<sup>4</sup>A. M. Ermolaev and R. N. Hewitt, *Nucl. Instrum. Methods B* **9**, 487 (1985).

<sup>5</sup>T. Mukoyama, C. D. Lin, and W. Fritsch, *Phys. Rev. A* **32**, 2490 (1985).

<sup>6</sup>Y. K. Kim, *Phys. Rev.* **154**, 17 (1967).

<sup>7</sup>T. Kagawa, *Phys. Rev. A* **12**, 2245 (1975).

<sup>8</sup>W. H. E. Schwarz and H. Wallmeier, *Mol. Phys.* **46**, 1045 (1982).

<sup>9</sup>W. Kutzelnigg, *Int. J. Quantum. Chem.* **25**, 107 (1984).

<sup>10</sup>H. Wallmeier, *Phys. Rev. A* **29**, 993 (1984).

<sup>11</sup>G. W. F. Drake and S. P. Goldman, *Phys. Rev. A* **23**, 2093 (1981).

<sup>12</sup>Y. Ishikawa, *Int. J. Quantum. Chem.* **18**, 375 (1984).

<sup>13</sup>S. P. Goldman, *Nucl. Instrum. Methods B* **9**, 493 (1985).

<sup>14</sup>P. Goldman, *Phys. Rev. A* **31**, 3541 (1985).

<sup>15</sup>S. P. Goldman and A. Dalgarno, *Phys. Rev. Lett.* **57**, 408 (1984).

<sup>16</sup>B. Gazdy and K. Ladanyi, *J. Chem. Phys.* **80**, 4333 (1984).

<sup>17</sup>T. Kagawa, *Int. J. Quantum. Chem.* **23**, 973 (1983).

<sup>18</sup>A. Liberman, D. T. Cromer, and J. T. Waber, *Phys. Rev. A* **137**, 27 (1965); *Comput. Phys. Commun.* **2**, 107 (1971).

<sup>19</sup>J. H. Scofield, *Phys. Rev.* **179**, 9 (1969).

<sup>20</sup>T. Mukoyama and T. Kagawa, *Phys. Rev. A* **29**, 1055 (1984).