PHYSICAL REVIEW A VOLUME 47, NUMBER 1 JANUARY 1993

Universal Gaussian basis set for accurate *ab initio* relativistic Dirac-Fock calculations

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(Received 28 August 1992)

A universal Gaussian basis set is developed for accurate *ab initio* relativistic Dirac-Fock calculations on atoms and molecules. The Dirac-Fock energies computed by using this single set of the universal Gaussian basis for the atoms, He ($Z=2$) through No ($Z=102$), are in excellent agreement with the corresponding numerical finite-difference Dirac-Fock method. The total Dirac-Fock energies for lighter atoms agree with the corresponding numerical limit to a part in 10^9 and for heavier systems to a part in 10^8. The total energy for the heaviest system, No ($Z=102$), calculated with our universal Gaussian basis set differs from the corresponding numerical limit by only 4 mhartrees.

PACS number(s): 31.10.+z, 31.15.+q, 31.20.Di, 31.30.Jv

I. INTRODUCTION

Ab initio relativistic calculations for atoms and molecules are carried out mostly within the finite-basis-set-expansion method. The choice of the appropriate set of basis functions is crucial because it ultimately determines the accuracy as well as the cost of the calculation. Among the types of functions employed in basis-set-expansion *ab initio* Dirac-Fock (DF) calculations are Slater-type functions (STF's) [1–5], orthogonal Laguerre functions [6–8], piecewise polynomials [9], and Gaussian-type functions (GTF's) [10–14]. Basis sets of STF's have been widely used for nonrelativistic calculations on both atoms and diatomic molecules because, in the point-nucleus approximation, they correctly represent the singularity at the point nucleus. Although the STF's with noninteger power of r have been used successfully in relativistic (point-nucleus) atomic calculations as they can reproduce the more severe relativistic cusp conditions at the point nucleus [3,4], they are not suitable for molecular DF calculations because of the difficulty of calculating the two-electron multicenter integrals. Therefore the use of GTF's in relativistic Dirac-Fock calculations has been investigated by a number of groups [10–17] because all the multicenter integrals over GTF can be evaluated exactly by closed formulas. A main disadvantage of GTF's relative to the STF's of noninteger power of r is that they provide a poor representation of the relativistic infinite cusp at the point nucleus. However, when the nucleus is represented more realistically by a finite body of uniform proton-charge distribution, it turns out that the solutions of the Dirac equation near the origin can be represented precisely by GTF's [18,19].

Since the computational cost of a finite basis set in atomic and molecular calculations increase as $\sim N^4$ (where N is the number of basis functions used), various attempts have been made to economize the cost as much as possible by adopting various strategies. One such approach was the introduction of a universal basis set [20] following the earlier work on the even-tempered STF and GTF basis sets [21]. It was observed that the optimum exponents of the rigorously optimized GTF's in Hartree-Fock atomic calculations could be related by a Gaussian rule [22]. The existence of such a rule suggested a high degree of universality in the optimized GTF representation for different atoms.

A universal basis set is a single, sufficiently flexible basis set which can be used for any atomic or molecular environment without much loss of accuracy. A major advantage of the use of universal GTF's over other varieties of GTF basis is that the transferability of all the one- and two-electron integrals over the universal GTF from system to system (with trivial multiplicative scale factors due to change in nuclear charges) leads to remarkable computational savings for nonrelativistic and relativistic calculations on atoms and molecules. Therefore there has been a considerable effort in designing the so-called universal Gaussian basis set [23–25]. In the present study, we have developed a single universal basis set of GTF's for accurate *ab initio* DF calculations for all the atoms, He ($Z=2$) through No ($Z=102$).

II. GENERATION OF UNIVERSAL GAUSSIAN BASIS SET FOR MATRIX DIRAC-FOCK CALCULATIONS

There is a great variety of GTF's one can use in atomic and molecular calculations. If the basis set of GTF's is sufficiently large and flexible, the particular choice of the GTF basis is not expected to be reflected in the calculated properties. One is forced, however, to use a moderately large basis set since its flexibility in general increases as it is extended. It is also well established that it is generally more profitable to increase the basis set size rather than optimize the individual basis function exponent, since the exponent optimization is computationally very costly.

The basis-set-exponent nonoptimization has been so far almost always the rule in relativistic quantum chemistry. The concept of a universal basis set arose from these considerations.

In the present study, we adopt this philosophy and construct a single, sufficiently flexible universal basis set of GTF for accurate relativistic DF calculations on the atoms, He ($Z=2$) through No ($Z=102$). In order to generate our universal basis set of GTF, the generator coordinate version of the Hartree-Fock method (GCHF) [23,24] is employed. This novel procedure was first applied to develop a universal GTF for nonrelativistic Hartree-Fock calculations on the He up to Xe atoms with reasonable success [24,25].

The GCHF method is characterized by the representation of the one-electron functions Ψ_i as an integral transform [23,24], viz.,

$$\Psi_i(1)=\int \phi_i(1,\alpha)f_i(\alpha)d\alpha, \quad i=1,2,\ldots,n \ , \tag{1}$$

where the ϕ_i are the generator functions. The f_i and α are the weight functions and the generator coordinate, respectively. The variations of the energy expectation value produce the Griffin-Wheeler-Hartree-Fock (GWHF) equations,

$$\int [F(\alpha,\beta)-\varepsilon_i S(\alpha,\beta)]f_i(\beta)d\beta=0, \quad i=1,2,\ldots,n \ . \tag{2}$$

The GWHF equations are integrated numerically through a discretization technique that preserves the integral character of the GCHF method, viz., the integral discretization (ID) technique [23]. The ID technique is implemented with a relabeling of the generator coordinate space through

$$\Omega=\frac{\ln\alpha}{A} \ , \quad A>1 \ . \tag{3}$$

An equally spaced N-point mesh $\{\Omega_i\}$ is selected so that one can obtain an adequate numerical integration range for the s, p, d, and f symmetries for several atoms. The integration range is then characterized by a starting point $\Omega_{\min}$, an increment $\Delta\Omega$, and N (number of mesh points). The scaling parameter A is chosen to be 6.0 as in a previous study [24]. The exponents of our universal basis of GTF's are generated by the following discretization parameters:

Symmetry	$\Omega_{\min}$	$\Delta\Omega$	N
s, p, d, and f	-0.64	0.12	32

These 32 exponents generated with the discretization parameters represent a single set of GTF exponents that can be applied for the DF calculations on the atoms, He ($Z=2$) up to No ($Z=102$). With this single set of universal Gaussian basis, the two-electron integrals need to be computed only once for use in all the DF calculations on the atoms, He ($Z=2$) up to No ($Z=102$).

Our matrix Dirac-Fock-Coulomb (DFC) and Dirac-Fock-Breit (DFB) self-consistent-field (SCF) calculations employ the finite-nucleus model of uniform proton-charge distribution discussed in Ref. [18]. The universal GTF's are chosen to satisfy the relativistic boundary conditions associated with the finite-nucleus model [18]. The GTF's that satisfy the boundary conditions associated with the finite nucleus automatically satisfy the condition of the so-called "kinetic balance" at the nonrelativistic limit [12].

III. RESULTS AND DISCUSSION

The DFC and DFB SCF calculations are performed on a number of closed-shell ground-state atoms, He ($Z=2$) through No ($Z=102$), using a universal Gaussian basis set. The finite-nuclear model of uniform proton-charge distribution and the kinetic balance condition are employed in all the calculations. The speed of light used in our DFC and DFB SCF calculations is 137.0370 a.u.

Table I displays the 32 exponents of the universal Gaussian basis generated in the manner described in the preceding section. The results of the matrix DFC and DFB SCF calculations are given in Table II. In this Table, E_{DFC}, E_{DFB} and E_{B} denote the DFC, DFB, and the variational Briet interaction energies, respectively. The variational Breit interaction energy E_{B} is computed as the difference between the E_{DFB} and E_{DFC}.

The results displayed in Table II show that the total DFC energies computed with our universal Gaussian

TABLE I. Basis-set exponents of the universal GTF.

0.021 494
0.044 157
0.090 718
0.186 374
0.382 893
0.786 628
1.616 074
3.320 117
6.820 958
14.013 204
28.789 191
59.145 470
121.510 418
249.635 037
512.858 511
1 053.633 557
2 164.619 772
4 447.066 748
9 136.201 616
18 769.716 020
38 561.127 946
79 221.261 891
162 754.791 419
334 368.848 683
686 938.467 338
1 411 269.200 969
2 899 358.315 629
5 956 538.013 185
12 237 309.514 749
25 140 735.076 029
51 649 961.080 194
106 111 395.371 615

TABLE II. Total Dirac-Fock-Coulomb (E_{DFC}), Dirac-Fock-Breit (E_{DFB}) and variational Breit interaction (E_{B}) energies (in hartrees).

Atom	Atomic mass	Basis-set size	E_{DFC}[a]	E_{DFB}[a]	E_{B}[a]	Finite difference (E_{DFC})[b]
He	4.0026	22*s*	−2.861 813 335	−2.861 749 572	0.000 063 763	−2.861 813 35
Be	9.0122	25*s*	−14.575 892 68	−14.575 189 47	0.000 703 21	−14.575 891 9
Ne	20.18	32*s*29*p*	−128.691 935 9	−128.675 295 1	0.016 640 8	−128.691 938
Mg	24.312	32*s*29*p*	−199.935 077 3	−199.032 502	0.031 827 1	−199.935 083
Ar	39.948	32*s*29*p*	−528.683 815 4	−528.551 492 4	0.132 323 0	−528.683 840
Ca	40.08	32*s*29*p*	−679.710 246 2	−679.519 251 8	0.190 994 4	−679.710 276
Kr	83.80	32*s*29*p*20*d*	−2 788.861 607	−2 787.435 714	1.425 893	−2 788.861 68
Sr	87.62	32*s*29*p*20*d*	−3 178.081 228	−3 176.362 668	1.718 560	−3 178.081 33
Xe	131.30	32*s*29*p*20*d*	−7 446.899 674	−7 441.129 882	5.769 792	−7 446.900 18
Ba	137.34	32*s*29*p*20*d*	−8 135.649 484	−8 129.104 066	6.545 418	−8 135.650 06
Hg	200.59	32*s*29*p*20*d*15*f*	−19 648.867 31	−19 626.234 65	22.632 66	−19 648.869 2
Rn	222.00	32*s*29*p*20*d*15*f*	−23 601.972 25	−23 572.620 63	29.351 62	−23 601.974 2
No	259.00	32*s*29*p*20*d*17*f*	−36 740.281 62	−36 685.136 48	55.145 14	−36 740.285 7

[a] This work (using the universal Gaussian basis set).

[b] E_{DFC} computed by using the Oxford numerical-finite-difference Dirac-Fock program [26].

basis set are in excellent agreement as compared to the corresponding numerical-finite-difference results. Our universal Gaussian basis set yields total DFC energies to within a few millihartrees (heavier atoms) or less (lighter atoms) of the corresponding numerical-finite-difference values.

The size of the universal Gaussian basis set in Table II indicates the number of exponents, for each *s*, *p*, *d*, and *f* symmetry, taken from the 32 universal GTF exponents shown in Table I. For each atom studied, we increased the number of exponents in each *s*, *p*, *d*, and *f* symmetry until obtaining a DFC energy value between the accuracy of microhartrees (for the lighter atoms) and millihartrees (for the heavier atoms) as compared to the numerical-finite-difference results (last column in Table II). Therefore, as one can see from Table II, for He we have obtained a DFC energy value within the accuracy of 10^{-8} hartrees, and for the case of Be our DFC energy value is slightly lower than the corresponding numerical-finite-difference value. For the heaviest atom studied, nobelium (No), we obtained a DFC energy value that differs from the corresponding finite-difference result by only 4 millihartrees. The DFC energy values computed by using our universal basis set of GTF's are consistently more accurate than the corresponding values computed by using the large geometrical Gaussian basis set [14], although the former is smaller in size than the latter.

Table III displays the DFC and DFB orbital energies of No ($Z=102$) obtained with our universal Gaussian basis set. The $1s_{1/2}$ orbital energy of No obtained by the DFB SCF is higher by 25.8 hartrees than that computed by the DFC SCF. For the $2s_{1/2}$ orbital the difference between the computed DFB and DFC orbital energies is about 3.3 hartrees. For $2p_{1/2}$ and $2p_{3/2}$ the DFB and DFC orbital-energy differences are 5.5 and 3.0 hartrees, respectively. As Mann and Johnson pointed out [27], the

TABLE III. Dirac-Fock-Coulomb (E_{DFC}) and Dirac-Fock-Breit (E_{DFB}) orbital energies of No (in hartrees).

Orbital	E_{DFC}[a]	E_{DFC}[b]	E_{DFB}[a]
$1s_{1/2}$	−5526.516	−5526.510	−5500.676
$2s_{1/2}$	−1082.793	−1082.790	−1079.535
$2p_{1/2}$	−1047.358	−1047.355	−1041.880
$2p_{3/2}$	−808.788 3	−808.787 9	−805.781 8
$3s_{1/2}$	−285.397 9	−285.396 7	−284.720 4
$3p_{1/2}$	−269.102 6	−269.101 3	−267.974 5
$3p_{3/2}$	−212.187 5	−212.187 1	−211.587 2
$3d_{3/2}$	−187.134 6	−187.134 1	−186.647 1
$3d_{5/2}$	−176.444 9	−176.444 5	−176.114 9
$4s_{1/2}$	−78.618 72	−78.618 09	−78.451 09
$4p_{1/2}$	−70.971 05	−70.970 35	−70.689 78
$4p_{3/2}$	−55.211 09	−55.211 11	−55.077 75
$4d_{3/2}$	−43.237 28	−43.236 99	−43.146 94
$4d_{5/2}$	−40.457 25	−40.457 33	−40.406 53
$4f_{5/2}$	−24.688 70	−24.688 30	−24.677 97
$4f_{7/2}$	−23.915 28	−23.914 98	−23.923 30
$5s_{1/2}$	−18.805 05	−18.805 06	−18.763 18
$5p_{1/2}$	−15.542 11	−15.542 24	−15.474 06
$5p_{3/2}$	−11.436 74	−11.437 31	−11.408 68
$5d_{3/2}$	−6.610 019	−6.610 473	−6.596 152
$5d_{5/2}$	−5.985 525	−5.986 144	−5.980 649
$5f_{5/2}$	−0.566 514 7	−0.566 945 9	−0.569 767 1
$5f_{7/2}$	−0.469 033 1	−0.469 441 2	−0.474 790 3
$6s_{1/2}$	−2.794 859	−2.795 121	−2.787 064
$6p_{1/2}$	−1.727 253	−1.727 562	−1.716 418
$6p_{3/2}$	−1.049 092	−1.049 447	−1.046 053
$7s_{1/2}$	−0.209 220 2	−0.209 317 9	−0.208 981 9

[a] This work (using the universal Gaussian basis set).

[b] Numerical DFC orbital energies computed by using the Oxford numerical-finite-difference Dirac-Fock program [26].

major effects of the inclusion of the Breit interaction term in the SCF process, for higher-Z systems, are the reorganization of the orbitals and a large shift in the inner-shell orbital energies. The DFB and DFC orbital-energy difference for the outer-shell orbitals of No presents a level shift much smaller in magnitude than for the inner-shell orbitals.

The orbital energies computed by the DFC SCF are, in general, lower than those computed by the DFB SCF; however, the orbital energies obtained by the DFB SCF calculation for the orbitals $4f_{7/2}$, $5f_{5/2}$, and $5f_{7/2}$ of No are slightly lower than those obtained by the DFC SCF. This same behavior was observed for some outer-shell orbitals of Rn in a previous paper [15]. The results in Table III show that the inclusion of the Breit interaction in the SCF process is essential for accurate calculations of the binding energies of the inner-shell electrons in systems with high Z.

The third column in Table III shows the numerical DFC orbital energies obtained by using the Oxford numerical-finite-difference Dirac-Fock program [26]. As one can see, the DFC orbital energies of the No atom obtained with the universal Gaussian basis set are in very good agreement with the corresponding numerical-finite-difference Dirac-Fock orbital energies [26].

IV. CONCLUSION

A major advantage of the GTF over the STF is that a large basis set of GTF's may by employed to achieve high accuracy without encountering the near-linear dependency problem reported with the STF basis sets [3,4]. The results clearly show that the variational determination of DF energies with the universal basis of GTF's is competitive in accuracy with the numerical-finite-difference DF approach. The present study demonstrates that it is indeed possible to obtain highly accurate *ab initio* DF energies for the atoms He ($Z=2$) through No ($Z=102$) by using a single set of universal Gaussian basis.

ACKNOWLEDGMENTS

G. L. Malli was supported in part by the Natural Sciences and Engineering Research Council of Canada through Grant No. A3598. A. B. F. Da Silva and G. L. Malli were supported in part by the Brazilian CNPq. Y. Ishikawa was supported in part by the National Science Foundation through Grant No. PHY-9008627. All grants are gratefully acknowledged. All the calculations were performed on an IBM RISC/6000 power station at Simon Fraser University.

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