An Efficient Computational Approximation to the Relativistic Self-Consistent-Field Method

Yoon Sup Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received July 10, 1986

Relativistic self-consistent-field (RSCF) calculations require considerably more computational time than corresponding nonrelativistic SCF (NRSCF) calculations because relativistic Dirac spinors have four components and because large component spinors and small component spinors span different spaces.[1] Basis sets in RSCF calculations are far larger than those in corresponding NRSCF calculations and thus the computation of integrals takes longer in RSCF than in NRSCF calculations. Dimensions of Fock matrices in RSCF calculations are also larger than those in corresponding NRSCF calculations. When an accurate RSCF result is desired, the computation time increases two orders of magnitude from NRSCF to RSCF calculations. Therefore, accurate RSCF calculations are affordable only for small systems even after numerical difficulties associated with too many functions in the same space is avoided. RSCF calculations that produce reliable, but not exact results still require about 20 times more computations than NRSCF calculations.[1]

Approximate methods that can significantly reduce the amount of computations in RSCF calculations are highly desirable. There are many approaches developed for these purposes, but most of them go beyond the theoretical framework of Dirac-Hartree-Fock (DHF) theory. In this paper, we describe an approximate RSCF (ARSCF) method which retains all the features of *ab initio* all-electron RSCF method. The present ARSCF method is similar to that used by Datta dn Ewig[2] except for differences in basis functions and in the definition of basis spinors.

Time consuming parts in RSCF calculations are computation of two electron integrals over basis functions and construction of Fock matrix in each iteration. Construction of Fock matrix takes a long time because two electron integrals have to be multiplied by proper density matrix at this stage. The size of the density matrix in a RSCF calculation is about 16 times larger than that of the comparable NRSCF calculation.[1] Compared with two electron parts, treatment of one electron terms is almost trivial in terms of computational time. When RSCF calculations are compared with NRSCF calculations, the source for most additional computational time for RSCF calculations can be attributed to handling of small component part. Therefore, significant savings can be achieved if two electron integrals containing small components can be neglected.

Since small components usually represent only tiny portion of electron densities, their contribution to Coulomb and exchange interactions are not expected to be substantial for most orbitals or spinors. It appears that reasonable RSCF results can be obtained even though we neglect Coulomb and exchange terms from small components. This is the ARSCF method tested here. One electron terms containing small components can not be neglected since small components are essential in producing relativistic kinetic energies, which are

the sum of kinetic energies and relativistic contributions, in DHF theory. The main assumption for this ARSCF method is that spinors produced without two electron interactions involving small components are reasonable approximations of correct spinors. When all the conditions are satisfied and the RSCF program is designed to take the full advantage of the present ARSCF method, computational time required in ARSCF calculations is the same as that in NRSCF for two electron integrals and only about twice as much as that in NRSCF calculations for Fock matrix construction. The dimension of Fock matrix for ARSCF calculations remains same as the full RSCF calculations and no saving is possible for diagonalization step, although it may possible that the convergence is reached in ARSCF calulation with fewer iterations than in RSCF calculations because of the simpler structure of two electron interactions in the former. When all these factors are combined, we may expect that ARSCF calculations will be at least an order of magnitude faster than the original RSCF calculations.

Although the present program is not structured to take advantage of this ARSCF method, we have calculated several ions of iodine ($Z = 53$) with this approximation and results are summarized in Table I. Since part of electron repulsion terms are neglected in ARSCF calculations, total energies of the system from ARSCF calculations are always lower than those from RSCF calculations as shown in Table 1. The differences become larger as the number of electrons increases, 0.06 a.u. for two electron to 14.5 a.u. for 28 electrons. Errors in total energies are not negligible in systems where relativistic effects are large. Estimate of relativistic contributions to total energies from ARSCF calculations are always larger than those from the original RSCF calculations since ARSCF method always produce the exactly same nonrelativistic limit energies as the RSCF calculations.

In most cases, we are not interested in total energies. Differences in energies and also other properties are usually the main interest in chemistry. In order to examine the validity of the ARSCF calculations for molecular properties, RSCF and ARSCF calculations have been carried out for IH at $R = 3.03$ a.u. and at $R = 3.5$ a.u. as shown in Table 2. The error in energy difference is quite small, 0.005 a.u., although total energies in RSCF and ARSCF calculations differ by 18 a.u.. It appears that the equilibrium bond lengths from ARSCF calculations will be shorter than those from corresponding RSCF calculations because the magnitude of difference between two calculations increases at shorter internuclear distances.

Omitted two electron interactions can be estimated by using spinors from ARSCF calculations. This requires computation of all two electron integrals omitted in the ARSCF calculation and can be viewed as an ARSCF method with corrections (ARSCFC). In ARSCFC caculations, savings of com-

Communications to the Editor

Bull. Korean Chem. Soc., Vol. 7, No. 6, 1986   481

Table 1. Total Energies (in a.u.) for Various Iodine (Z = 53) ions from RSCF and ARSCF Calculations. In ARSCFC Calculations, two Electron Contributions of Small Components Computed with ARSCF Orbitals are Added in ARSCF Energies

No. of electrons	RSCF	ARSCF	ARSCFC
2	– 2887.5170	– 2887.5689	– 2887.5170
4	– 3572.7313	– 3573.8593	– 3572.7311
10	– 5349.1809	– 5355.1744	– 5349.1744
28	– 6818.0352	– 6832.5170	– 6818.0057

Table 2. Total Energies (in a.u.) for IH at R = 3.03 a.u. and R = 3.5 a.u. from RSCF, ARSCF and ARSCFC Calculations

R	RSCF	ARSCF	ARSCFC
3.03	– 7115.7980	– 7133.7457	– 7115.7673
3.5	– 7115.7819	– 7133.7246	– 7115.7501
ΔE	– 0.0161	– 0.0211	– 0.0172

* ΔE = E(R = 3.03) – E(R = 3.5).

putation compared with RSCF method are only in constructing Fock matrix in each iteration. If the SCF procedure needs many iterations, these savings will also be significant. Actually, the construction of Fock matrix in each iteration is the most time consuming step in RSCF calculations. Results of ARSCFC calculations are also shown in Table 1 and 2. Differences in total energies are much smaller in both cases indicating that spinors from ARSCF calculations are very good approximations to those from RSCF calculations. The largest difference between RSCF and ARSCFC total energies is 0.03

a.u. for IH. Furthermore, most of this difference is in core orbitals since the difference for 28 electron I ion is already 0.029 a.u. as shown in Table 1.

We believe that molecular properties obatainable by ARSCFC calculations are very close to those calculated by the corresponding RSCF calculations and the spinors from ARSCF calculations are quite reliable approximations to those from the RSCF calculations.

In conclusion, ARSCF calculations will be useful for systems containing only light atoms, where relativistic effects are not significant, without any further corrections and can be used as practical methods for generating reasonable RSCF spinors for most molecules. The ARSCF method can be implemented to perform very efficient relativistic calculations. Computational advantages for ARSCFC are not so much as those for ARSCF method but still substantial when compared with the original RSCF method. ARSCFC results closely duplicate the RSCF results and further study will suggest various techniques applicable to ARSCFC method for greatly improving efficiency.
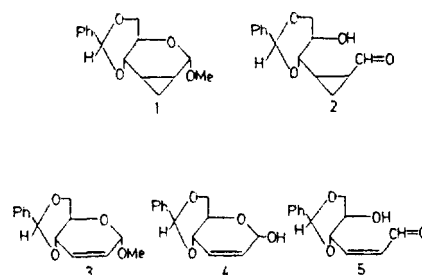
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Selective Hydrolysis of Methyl 4,6-O-Benzylidene-2,3-dideoxy-α-D-erythro-2-enopyranoside in the Presence of Rh(Ph₃P)₃Cl or Pd/C

Kwan Soo Kim*, Kyu Seong Jung, and Chi Sun Hahn

Department of Chemistry, Yonsei University, Seoul 120. Received July 23, 1986

The unsaturated sugars are versatile synthons for a diverse array of saccharide derivatives.[1,2] The extensive investigations, especially by Fraser–Reid and coworkers,[3] have been done on the reactions of unsaturated sugars and their synthetic utilities have been domonstrated. Fraser–Reid and coworkers have reported that a cyclopropanated pyranoside 1 were readily hydrolyzed by refluxing in aqueous dioxane for 1hr to afford a cyclopropyl aldehyde 2.[4] The ease of the hydrolysis was ascribed to formation of a cyclopropylcarbinyl oxocarbonium ion.[5] However, the same workers failed to obtain a hemiacetal 4 or an α,β-unsaturated aldehyde 5 from methyl 4,6-O-henzylidene-2,3-O-dideoxy-α-D-erythro-2-enopyranoside (3), the 2-olefin equivalent of 1 upon hydrolysis. They obeserv-

ed that benzaldehyde was liberated to give unknown compounds.[6]