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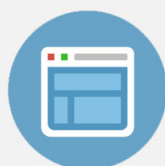
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# Relativistic self-consistent-field methods for molecules. II. A single-determinant Dirac-Fock self-consistent-field method for closed-shell polyatomic molecules<sup>a)</sup>

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The single-determinant Dirac-Fock self-consistent-field method is applied to closed-shell polyatomic molecules and numerical calculations are performed on H<sub>2</sub>, LiH, Li<sub>2</sub>, HF, F<sub>2</sub>, and H<sub>2</sub>CO. The Gaussian-type functions are employed to express the molecular spinors. Nonrelativistic calculations are also made using the equation of the nonrelativistic limit of the Dirac-Fock equation.

## I. INTRODUCTION

In the preceding paper,<sup>1</sup> which will be referred to as I, a general Dirac-Fock multiconfiguration self-consistent field (SCF) theory is presented. As a special case of the general theory, the single-determinant Dirac-Fock SCF method is applied to closed-shell linear molecules and preliminary calculations on H<sub>2</sub> and LiH are given using the Slater-type basis functions.

In the present paper, the single-determinant Dirac-Fock SCF method for linear molecules in I is extended for closed-shell polyatomic molecules of general shapes. For linear molecules the matrix elements in the Dirac-Fock equations are evaluated in terms of Slater-type functions without undue difficulty. However, for general polyatomic molecules the integrals over Slater-type functions are not easily computed. Thus, in the present paper, the Gaussian-type functions are employed as basis functions and numerical calculations have been performed.

In Sec. II, the SCF method relevant to the present calculations is given, of which the large part is developed in I. In Sec. III, the numerical results are reported on H<sub>2</sub>, LiH, Li<sub>2</sub>, HF, F<sub>2</sub>, and H<sub>2</sub>CO and a discussion of the method and the results is also given.

## II. DIRAC-FOCK MATRIX SCF EQUATION AND ITS NONRELATIVISTIC LIMIT

We consider an  $N$ -electron molecular system whose wave functions are described by single antisymmetrized products of four-component molecular spinors. The molecular spinors  $\{\phi_i; i=1, 2, \dots, N\}$  are expanded in terms of four-component basis spinors  $\{\chi_p, p=1, 2, \dots, n\}$  as

$$\phi_i = \sum_{p=1}^n \chi_p C_{ip}, \quad (2.1)$$

where the expansion coefficients  $\{C_{ip}\}$  are assumed to be scalars.

The Dirac-Fock matrix SCF equation take the form as

$$\mathbf{F}\mathbf{c}_i = \epsilon_i \mathbf{S}\mathbf{c}_i. \quad (2.2)$$

The matrix elements in Eq. (2.2) are defined in Eqs. (2.34)–(2.38) of I. For general polyatomic molecules the matrix elements takes complex values as do the expansion coefficients. The relativistic total energy is written in Eq. (2.39) of I.

If we write the molecular spinors as

$$\phi_i = \sum_{p=1}^{n^L} C_{ip}^L \begin{bmatrix} \chi_p^L \\ 0 \\ 0 \end{bmatrix} + \sum_{q=1}^{n^S} C_{iq}^S \begin{bmatrix} 0 \\ 0 \\ i\chi_q^S \end{bmatrix}, \quad (2.3)$$

where  $\{C_{ip}^L\}$  and  $\{C_{iq}^S\}$  are assumed to be scalars and  $\chi_p^L$  and  $i\chi_q^S$  are upper and lower two components of the four-

TABLE I. Gaussian expansions for H.

Basis set	$nl$	Orbital exponent	$1s_{1/2}$ Coefficient
A. Large component			
1	1s	3.24402	0.103895
	1s	0.529693	0.479599
	1s	0.128260	0.549774
2	1s	7.97926	0.0346569
	1s	1.34977	0.195086
	1s	0.337963	0.524235
	1s	0.102017	0.387015
	1s	82.0488	0.00210511
3	1s	11.8864	0.0164180
	1s	2.65518	0.0821548
	1s	0.741502	0.276136
	1s	0.240217	0.502504
	1s	0.0848211	0.264642
	1s	0.0848211	0.264642
B. Small component			
4	2p	2.89791	-0.138651
	2p	0.347991	-0.292294
5	2p	9.00942	-0.0602107
	2p	1.24197	-0.174972
	2p	0.233258	-0.229994
6	2p	25.1484	-0.0282674
	2p	3.65279	-0.0847722
	2p	0.747307	-0.187394
	2p	0.178307	-0.177489
7	2p	57.5813	-0.0150671
	2p	8.68862	-0.0445343
	2p	1.90735	-0.108299
	2p	0.494054	-0.186488
	2p	0.140357	-0.129508

<sup>a)</sup>Presented at the Third International Congress of Quantum Chemistry held in Kyoto, Japan, during Oct. 28–Nov. 3, 1979.

TABLE II. Gaussian expansions for Li.

Basis set	$nl$	Orbital exponent	$1s_{1/2}$ Coefficient	$2s_{1/2}$ Coefficient
A. Large component				
1	1s	55.9765	0.0414807	-0.00517174
	1s	9.64437	0.206042	-0.0398047
	1s	2.39935	0.498173	-0.0765397
	1s	0.689496	0.405889	-0.186995
	1s	0.0567299	0.0114492	1.02110
2	1s	55.9765	0.0415569	-0.00658178
	1s	9.64437	0.205719	-0.0337631
	1s	2.39935	0.499135	-0.0943716
	1s	0.689496	0.404145	-0.155676
	1s	0.0601244	0.0178133	0.796261
	1s	0.0195522	-0.00813790	0.288962
B. Small components				
3	2p	16.6707	-0.461165	0.0706360
	2p	2.16942	-0.708004	0.156057
	2p	0.0401664	-0.122006	-0.127005
4	2p	51.8075	-0.218064	0.0355370
	2p	7.54085	-0.509069	0.0798258
	2p	1.45812	-0.541187	0.136221
	2p	0.0446874	-0.0598867	-0.132321

component basis spinors  $\chi_p$ , respectively, and retain the terms of  $c^0$ , the zeroth order of the speed of light, in the Dirac-Fock Eq. (2.2), we obtain the equation for the nonrelativistic limit as

$$[\mathbf{F}^{LL} + \mathbf{X}] \mathbf{c}_i^L = \epsilon_i \mathbf{S}^L \mathbf{c}_i^L, \quad (2.4)$$

where

$$\mathbf{X} = -\mathbf{T}^{LS} (\mathbf{S}^S)^{-1} \mathbf{T}^{SL} / 2. \quad (2.5)$$

The matrix elements in Eqs. (2.4) and (2.5) are defined by Eqs. (3.8)–(3.19) in I. The total energy of the system in this approximation, the nonrelativistic energy, is written as

$$E = H_0 + \sum_{pq} (U_{pq}^L + X_{pq}^{SL}) D_{pq}^{LL} + \frac{1}{2} \sum_{pqrs} D_{pq}^{LL} (J_{pq,rs}^{LL} - K_{pq,rs}^{LL}) D_{rs}^{LL}, \quad (2.6)$$

where the repulsive energy between nuclei in the system  $H_0$  is written as Eq. (2.2) of I, the nuclear potential terms  $U_{pq}$  are defined by Eq. (3.16) of I, and the density matrices  $D_{pq}$  by Eq. (3.20) of I. Equation (2.4) is an extension from the one derived by Kim,<sup>2</sup> who assumed that  $n^L = n^S$ . [See also Eq. (4.6) in I.] If we use a complete set of two-component basis spinors  $\{\chi_p^S\}$  to express the molecular spinors in Eq. (2.3), the matrix elements defined by Eq. (2.5) are reduced to the ones over the kinetic energy operator

$$(\mathbf{X})_{pq} = \langle \chi_p^L | -\frac{1}{2} \nabla^2 | \chi_q^L \rangle,$$

since

$$\sum_{rs} |\chi_r^S\rangle (\mathbf{S}^{S-1})_{rs} \langle \chi_s^S| = 1$$

and  $(\sigma \cdot \nabla)^2 = \nabla^2 \mathbf{I}$ , where  $\mathbf{I}$  is  $2 \times 2$  unit matrix. Hence, Eq. (2.4) is reduced to the nonrelativistic Hartree-Fock equation. If we use a complete or a near complete set of two components basis spinors for the small components of the molecular spinors, the energy calculated by Eq. (2.6) gives the nonrelativistic Hartree-Fock energy. However, even if the basis set used is complete, the "nonrelativistic" wave functions obtained by Eq. (2.4) consist of the four-component spinors and the states are labeled by the double group.

TABLE III. Relativistic and nonrelativistic energies of  $H_2$ .

Basis functions		Relativistic calc.		Nonrelativistic calc.		Relativistic energy (eV)
Large comp.	Small comp.	- TE <sup>a</sup>	- $\epsilon^b$	- TE <sup>a</sup>	- $\epsilon^b$	
Minimal basis sets						
(3) <sup>c</sup>	(2) <sup>d</sup>	1.109268	0.62893	1.109262	0.62892	- 1.5 × 10 <sup>-4</sup>
(3)	(3)	1.096739	0.62266	1.096733	0.62266	- 1.6 × 10 <sup>-4</sup>
(3)	(4)	1.090456	0.61952	1.090449	0.61952	- 1.6 × 10 <sup>-4</sup>
(3)	(5)	1.089336	0.61896	1.089329	0.61896	- 1.6 × 10 <sup>-4</sup>
Semidouble basis sets						
(3,1)	(2)	1.134549	0.59749	1.134540	0.59748	- 2.5 × 10 <sup>-4</sup>
(3,1)	(3)	1.138426	0.57772	1.138415	0.57771	- 2.8 × 10 <sup>-4</sup>
(3,1)	(4)	1.150566	0.57442	1.150555	0.57443	- 2.9 × 10 <sup>-4</sup>
Extended basis sets						
(3,1)	(1,1)	1.132063	0.60040	1.132054	0.60041	- 2.5 × 10 <sup>-4</sup>
(3,1)	(1,2)	1.134804	0.57986	1.134791	0.57984	- 3.3 × 10 <sup>-4</sup>
(4,1,1)	(2,1,1)	1.119366	0.59169	1.119353	0.59168	- 3.7 × 10 <sup>-4</sup>
(3,1,1,1)	(2,1,1,1)	1.117704	0.58996	1.117690	0.58995	- 3.7 × 10 <sup>-4</sup>

<sup>a</sup>Total energy in a.u.

<sup>b</sup>Spinor energy in a.u.

<sup>c</sup>Gaussian expansions for large components of  $1s_{1/2}$ . 1s-type Gaussians are used. (See Table IA.)

<sup>d</sup>Gaussian expansions for small components of  $1s_{1/2}$ . 2p-type Gaussians are used. (See Table IB.)

TABLE IV. Relativistic and nonrelativistic energies of LiH, Li<sub>2</sub>, HF, F<sub>2</sub>, and H<sub>2</sub>CO.

Basis functions		Relativistic calc.			Nonrelativistic calc.		Relativistic energy (eV)
Large comp.	Small comp.	-TE <sup>a</sup>	-ε <sup>b</sup>		-TE <sup>a</sup>	-ε <sup>b</sup>	
LiH							
Li (5, 5) <sup>c</sup>	(3, 3) <sup>d</sup>	8.181743	(E <sub>1/2</sub> ) <sup>e</sup>	2.56044	8.181141	2.56066	-0.016
H (3) <sup>f</sup>	(2) <sup>g</sup>		(E <sub>1/2</sub> )	0.30225		0.31365	
Li (6, 6)	(4, 4)	7.984371	(E <sub>1/2</sub> )	2.47454	7.983637	2.47420	-0.020
H (3)	(3)		(E <sub>1/2</sub> )	0.29614		0.29632	
Li (6, 4, 2)	(4, 4)	8.060037	(E <sub>1/2</sub> )	2.57561	8.05921	2.57531	-0.023
H (3, 1)	(2)		(E <sub>1/2</sub> )	0.31272		0.31272	
Li <sub>2</sub>							
Li (6, 4, 2)	(4, 4)	15.518358	(E <sub>1/2g</sub> )	2.60737	15.515984	2.60715	-0.065
			(E <sub>1/2g</sub> )	0.76822		0.76794	
			(E <sub>1/2u</sub> )	0.49238		0.49213	
HF							
H (3)	(3)	100.31257	(E <sub>1/2</sub> )	26.18709	100.22568	26.15307	-2.4
F (6, 6/6, 6) <sup>h</sup>	(6, 6/6/3) <sup>i</sup>		(E <sub>1/2</sub> )	1.56555		1.56217	
			(E <sub>1/2</sub> )	0.73356		0.73363	
			(E <sub>3/2</sub> )	0.67456		0.67490	
			(E <sub>1/2</sub> )	0.62483		0.62326	
F <sub>2</sub>							
F (6, 6/6, 6)	(6, 6/6/3)	199.37822	(E <sub>1/2g</sub> )	26.49962	199.20545	26.46412	-4.7
			(E <sub>1/2u</sub> )	26.49077		26.45516	
			(E <sub>1/2g</sub> )	1.77679		1.77309	
			(E <sub>1/2u</sub> )	1.51695		1.51242	
			(E <sub>3/2u</sub> )	0.88329		0.88315	
			(E <sub>1/2u</sub> )	0.84709		0.84595	
			(E <sub>1/2g</sub> )	0.81207		0.81250	
			(E <sub>3/2g</sub> )	0.75281		0.75257	
			(E <sub>1/2g</sub> )	0.68110		0.67795	
H <sub>2</sub> CO							
H (3)	(3)	113.8641	(E <sub>1/2</sub> )	20.61280	113.7970	20.593	-1.8
C (6, 6/6, 6) <sup>h</sup>	(6, 6/6/2) <sup>i</sup>		(E <sub>1/2</sub> )	11.58757		11.580	
O (6, 6/6, 6) <sup>h</sup>	(6, 6/6/2) <sup>i</sup>		(E <sub>1/2</sub> )	1.47080		1.470	
			(E <sub>1/2</sub> )	0.91469		0.914	
			(E <sub>1/2</sub> )	0.78357		0.7843	
			(E <sub>1/2</sub> )	0.70420		0.7049	
			(E <sub>1/2</sub> )	0.63284		0.6335	
			(E <sub>1/2</sub> )	0.51138		0.5110	

<sup>a</sup>Total energy in a.u.<sup>b</sup>Spinor energy in a.u.<sup>c</sup>Gaussian expansions for large components (GL) of 1s<sub>1/2</sub> and 2s<sub>1/2</sub>. 1s-type Gaussians are used. (See Table IIA.)<sup>d</sup>Gaussian expansions for small components (GS) of 1s<sub>1/2</sub> and 2s<sub>1/2</sub>. 2p-type Gaussians are used. (See Table IIB.)<sup>e</sup>Double group symmetry in Herzberg's notation (Ref. 10 in the text).<sup>f</sup>See footnote a of Table III.<sup>g</sup>See footnote d of Table III.<sup>h</sup>GL of 1s<sub>1/2</sub>, 2s<sub>1/2</sub>, 2p<sub>1/2</sub>, and 2p<sub>3/2</sub>. 1s- and 2p-type Gaussians are used.<sup>i</sup>GS of 1s<sub>1/2</sub>, 2s<sub>1/2</sub>, 2p<sub>1/2</sub>, and 2p<sub>3/2</sub>. 2p-, 1s-, and 3d-type Gaussians are used.

### III. NUMERICAL CALCULATIONS

Preliminary calculations have been performed on H<sub>2</sub>, LiH, Li<sub>2</sub>, HF, F<sub>2</sub>, and H<sub>2</sub>CO. This section gives the details of the calculations and results.

#### A. Basis functions

For general polyatomic molecules, the multicenter integrals, which appear in the matrix SCF Eq. (2.2), cannot be easily evaluated if we use Slater-type func-

tions employed in I. We have adopted Gaussian-type functions for which we can calculate the integrals analytically. Thus, the basis functions employed in Eq. (2.3) are

$$\eta(\mathbf{r}; n, l, m) = \left[ \sum_{i=1}^N c_i R_{ni}(\mathbf{r}; \alpha_i) \right] Y_{lm}(\theta, \varphi), \quad (3.1)$$

where

$$R_{ni}(\alpha_i) = N_n(\alpha_i) r^{n-1} \exp(-\alpha_i r^2),$$

$$N_n(\alpha) = 2^{n+1} [(2n-1)!]^{-1/2} (2\pi)^{-1/4} \alpha^{(2n+1)/4},$$

and  $Y_{lm}(\theta, \varphi)$  is spherical harmonic.<sup>3</sup>

We have generated the Dirac-Fock atomic wave functions for the generalized average of configurations using Desclaux's program<sup>4</sup> and fitted them in terms of Gaussians [Eq. (3.1)] by the method of least squares.<sup>5</sup> As shown in I, we need the basis functions having  $n=l$  quantum numbers to represent the small components of the atomic wave functions with quantum numbers  $j = l + 1/2$ . However, since the analyses on the Gaussians having  $n=l$  quantum numbers have not yet been done, we have approximated them by the Gaussians having  $n = l + 1$  quantum numbers. The Gaussian expansions of H and Li are shown in Tables I and II.

## B. Organization of program

The program consists of two parts. In the first part, we calculate the integrals over the basis spinors and store them on files. Then, in the second part, we solve the Dirac-Fock Eq. (2.2) and its nonrelativistic limit [Eq. (2.4)].

Although there exist the integral analyses over spherical Gaussians<sup>6</sup> defined in Eq. (3.1), the computer programs we have are based on the one for Cartesian Gaussians.<sup>7</sup> In the first part, we compute the nonzero and nonredundant integrals over Cartesian Gaussians and transform them directly to those over basis spinors, bypassing the transformation from the Cartesian to the spherical Gaussians. In the second part, we construct the Dirac-Fock matrix in Eq. (2.2) using the integrals calculated in the first part and solve the eigenvalue problems following the usual iterative procedure. Since the matrix elements take complex values, we have to solve general Hermitian eigenvalue problems. Initial input vectors in the iterative process were guessed by the nonrelativistic *ab initio* wave functions. We also solve the nonrelativistic limit of the Dirac-Fock Eq. (2.4) and calculate the nonrelativistic total energy using Eq. (2.6).

## C. Calculated results and discussion

We have solved the Dirac-Fock Eq. (2.2) and its nonrelativistic limit [Eq. (2.4)] and computed the total energies of the systems using Eqs. (2.39) of I and Eq. (2.6) of this paper. The following constants are employed: the velocity of light  $c = 137.0388$  a.u., 1 bohr  $= 0.5291672$  Å, and 1 hartree  $= 27.21$  eV. The relativistic energies have been obtained by subtracting the nonrelativistic total energies [Eq. (2.6)] from the relativistic total energies [Eq. (2.39) of I]. In the course of this

work, we found that when the nonrelativistic *ab initio* Hartree-Fock energy is used as the above nonrelativistic total energy, the calculated relativistic energy turns out to be unreasonably large. Hence, we have not adopted this scheme of calculating the relativistic energies; as we have seen in Sec. II, it would be preferable to use Eq. (2.6) as the nonrelativistic energy if we employ an incomplete set of basis spinors.

We have performed several calculations on H<sub>2</sub> molecule whose bond distance is assumed to be 0.74 Å.<sup>9</sup> Table III shows the calculated energies. With the improvement of the basis sets, the calculated relativistic energies converge to  $-3.7 \times 10^{-4}$  eV. This value is reasonable if we consider that the atomic relativistic energy of H atom is  $-1.8 \times 10^{-4}$  eV.<sup>8</sup>

We have also carried out the calculations on LiH, Li<sub>2</sub>, HF, F<sub>2</sub>, and H<sub>2</sub>CO using minimal and semi-double-zeta basis sets. The following bond lengths are adopted<sup>9,10</sup>: Li-H = 1.5949 Å, Li-Li = 2.672 Å, H-F = 0.9171 Å, F-F = 1.435 Å, C-O = 1.210 Å, and H-C = 1.102 Å. For H<sub>2</sub>CO (formaldehyde) we have assumed C<sub>2v</sub> geometry and the bond angle  $\angle$ HCH adopted in the calculations is 121.1°. The calculated results are shown in Table IV. Even if the minimal basis sets are adopted, reasonable values are obtained for the relativistic energies; the atomic relativistic energies of Li, C, O, and F are -0.022, -0.444, -1.518, and -2.509 eV,<sup>11</sup> respectively. Some of the  $\pi$ -orbital energies of HF and F<sub>2</sub> calculated by the nonrelativistic Eq. (2.4) have turned out nondegenerate. This is due to the incomplete basis sets employed.

Finally, we mention some difficulties in performing the Dirac-Fock calculations in the framework of the basis set expansion method, which we have encountered in the preceding<sup>1</sup> and the present works. The biggest, and only one, difficulty is associated with the fact that we need about four times as many basis functions in comparison to the nonrelativistic calculations. Hence, we need a lot of computer time to compute the molecular integrals and need large file spaces to store intermediate data. We need some sophistication in the programming. Other difficulties we have had are those minors as the diagonalization of the Dirac-Fock matrices of complex values, the increased number of SCF iterations, etc.

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