All-Electron Relativistic SCF Calculations for Light Atoms and Diatomic Molecules; Correct Nonrelativistic Limit Calculations with a Relativistic Method

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Procedures to perform reliable relativistic self-consistent-field (RSCF) calculations are described. Using light atoms and molecules, it is demonstrated that the present method always yields correct nonrelativistic limit by employing a sufficiently large value for the speed of light in RSCF calculations. Many problems associated with analytic expansions of the Dirac equations can be computationally avoided by kinetically balancing the basis sets for large and small component spinors. Results of RSCF calculations for Ne, Kr, H_2, and LiH indicate very small relativistic effects for these systems as expected. Trends found is these molecules, however, may be useful in understanding relativistic effects for molecules with similar valence electronic structures and heavier atoms.

Introduction

The electronic structure and properties of heavy atom containing molecules are not accurately computed without considering relativistic effects. There are excellent review articles[1-3] clearly demonstrating the importance of relativistic contributions for molecules. In one-electron systems, relativistic corrections are properly accounted for by the Dirac equation. The obvious extension to n-electron systems would be to use a Hamiltonian which adds the electron repulsion terms to the Dirac operators for individual electrons. When the wave function is approximated by a Slater determinant, the above Hamiltonian leads to the Dirac-Hartree-Fock (DHF) method. Although the DHF method suffers from some theoretical difficulties caused by negative mass solutions of the Dirac operator,[3,4] its numerical solutions have been successfully used in the study of atoms.[5] Considering difficulty in obtaining numerical Hartree-Fock (HF) solutions even in the nonrelativistic case, the basis set expansion method is the practical way to obtain the DHF wave functions for molecules. The DHF wave functions are complete basis set limits in the expansion methods just as nonrelativistic HF (NRHF) wave functions are the complete basis set limits of nonrelativistic self-consistent-field (NRSCF) calculations. Therefore, we will refer basis set expansion DHF calculations as a relativistic self-consistent-field (RSCF) calculations. In this paper, we present discussion about RSCF methods using calculational results for atoms and diatomic molecules.

In the previous paper,[6] we have reported the first attempt to perform all-electron RSCF calculations on heavy atom containing molecules, demonstrating that it is possible to make estimates of DHF qualities for molecular properties like D_e and R_e for AgH and AuH. The careful analyses based upon well designed all-electron RSCF calculations are useful not only in understanding the relativistic effects but also in evaluating various approximate methods, *i.e.*, effective core potential,[7] one-center expansion,[8] local density,[9,10] and discrete basis set[11] method, utilized in the study of relativistic effects for molecules. In addition, a RSCF method can easily be extended to more elaborate methods such as those including correlation effects or higher order relativistic corrections. Therefore, it is highly desirable to establish reliable and efficient RSCF procedures for molecular studies and to perform a large number of all-electron RSCF calculations for molecules.

In addition to the existence of negative mass solutions to the Dirac equation, which are also called positron solutions, the basis set expansions of DHF method posses a number of theoretical and computational difficulties.[4] One most important difficulty is in obtaining correct kinetic energies from the velocity operator. This problem has been the subject of many recent theoretical studies and can be avoided by using basis sets satisfying 'kinetic balance' condition.[12-16] We have also presented the recipe for generating basis sets with kinetic balance in our earlier papers and used the concept as a guideline in designing our basis set of Ag and Au.[6] We have performed relativistic and correct nonrelativistic limit RSCF calculations for several light atoms and diatomic molecules with Slater-type basis functions, and the results are discussed in this report.

The main purpose of this paper is to raise theoretical and computational questions about RSCF methods for molecules and to provide practical solutions to these questions. Although there have been some attempts to perform all-electron RSCF calculations for heavy atom containing molecules other than our AgH and AuH calculations,[17] we think that the present procedure is one of the most efficient RSCF methods available. Therefore, a clear description of our approach and the result of test calculations could be useful in designing an efficient RSCF procedure in the future, especially in view that there are considerable amounts of computational difficulties other than achieving the kinetic balance in performing RSCF calculations for molecules. In addition to earlier papers[18,19] describing RSCF method for molecules in principle without analysing such practical difficulties, procedures and results of RSCF calculations for atoms with Gaussian-type basis functions are also reported by Matsuoka and coworker.[20]

The brief description of the present RSCF method is given in the next section with important computational considerations. This section about the computational method is followed by the section summarizing the result of calculations for Ne, Kr, LiH, and H_2. Atomic calculations provide useful checks for the symmetry property of molecular RSCF program and are crucial in developing theoretical concepts. Summary and discussions are given in the last section.

Theory and Computational Method

The formalism for DHF theory is essentially the same as that for nonrelativistic HF theory except that the one electron wave function is a four component spinor in DHF theory. Basis set expansion methods for DHF calculations have been first given for atoms by Kim[21] and then for molecules by several workers.[6,22,23] A description of the present RSCF method is also available from the previous report[6] and we summarize the essential features for the clarity of presentation.

The relativistic Hamiltonian, H_R, for molecules is given be

$$H_R=\sum_i h_D(i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}+\frac{1}{2}\sum_{I\neq J}\frac{Z_IZ_J}{R_{IJ}}, \tag{1}$$

where i, j label electrons from 1 to n, and I, J label nuclei from 1 to N, with the second and the third terms are repulsion terms between electrons and nuclei, respectively, and other terms have their usual meaning.[21] The Dirac operator h_D is the relativistic operator for one-electron term and can be written in atomic unit (a.u.) as

$$h_D(i)=c\ \alpha_i\cdot p_i+c^2\beta'-\sum_{I=1}^{N}\frac{Z_I}{r_{ij}}, \tag{2}$$

where c is the speed of light, α is a vector whose three components are 4×4 matrices,

$$\alpha_x=\begin{bmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{bmatrix},\quad \alpha_y=\begin{bmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{bmatrix},$$

$$\alpha_z=\begin{bmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\1&-1&0&0\end{bmatrix}, \tag{3}$$

p is the linear momentum operator with three components $-i(\partial/\partial x)$, $-i(\partial/\partial y)$, $-i(\partial/\partial z)$, and β' is the matrix

$$\beta'=\begin{bmatrix}0&0&0&0\\0&0&0&0\\0&0&-2&0\\0&0&0&-2\end{bmatrix}, \tag{4}$$

which is redefined from the rest mass energy term so that the energy spectra of electrons appear near zero rather than near c^2 in atomic unit. The energies of negative mass solutions appear near $-2c^2$ with the above definitions.

By using the above relativistic Hamiltonian, many-electron relativistic interactions are not included. These additional relativistic contributions[4] are usually much smaller than those accounted for by the Hamiltonian of Eq. (1) and can be added as perturbations after reasonable wave functions are obtained as done in atoms.[5] Without making any further justifications about the imporance of many-electron relativistic effects, we will limit our discussions on applying H_R of Eq. (1) for closed-shell states of diatomic molecules and atoms with single configuration approximation.

In the DHF theory, the wave function for a closed-shell configuration is approximated by

$$\Psi=(n!)^{-\frac{1}{2}}\,Det|\phi_1(1)\phi_2(2)\cdots\phi_n(n)|, \tag{5}$$

where $\phi_i(i)$ is a four component spinor and $<\phi_i|\phi_j>=\delta_{ij}$. Each molecular or atomic spinor (MS or AS), $\phi_i(i)$, is approximated by a linear combination of four component basis spinors (BS)

$$\phi_i=\sum_{p=1}^{m}\chi_p^{BS}C_{pi}, \tag{6}$$

where χ_p^{BS} is a basis spinor and C_{pi} refers to the expansion coefficient of χ_p^{BS} for ϕ_i. The expansion coefficients, C_{pi}'s can be determined from the Dirac-Fock[24] equation, which is the relativistic analog of the Fock equation,

$$FC=\varepsilon SC, \tag{7}$$

where F is a relativistic Fock matrix defined by integral of terms in H_R of Eq. (1) between basis spinors, χ_p^{BS}'s, and proper density matrix, constructed from C. The dimensions of matrices in Eq. (7) are the same as the number of basis spinors, m, but the dimension is significantly reduced when the equivalence condition or the pairing requirement for spinors within the same shell is imposed.[22] The expression for the total energy is similary simplified.[6]

In the axial symmetry, molecular states in DHF theory are described by ω-ω coupling scheme[22,25] analogous to j-j coupling for atoms. Each spinor belongs to an irreducible representation of double group with half-integer value of ω and spinors with $m_\omega=\pm\omega$ constitute a degenerate pair and a shell. In other symmetries lower than the axial symmetry, ω is not a good quantum number, but all shells are still composed of pair of spinors.[26] The Fock matrix F can be brought into a block structure by imposing equivalence restrictions for spinor pairs and symmetry groupings. Both of these conditions are fully utilized in the present RSCF method in order to reduce the amount of computation.[6]

Each four component basis spinor in Eq. (6), χ_p^{BS}, is allowed to have only one non-zero component which is represented by a Slater type function (STF), χ_p,

$$\chi_p(n_p,\ l_p,\ m_p,\ \zeta_p)=Nr^{n_p-1}\exp(-\zeta_p r)Y_{l_pm_p}(\theta,\ \varphi), \tag{8}$$

where index p runs over the basis functions, N is a normalization factor, and Y_{lm} is a spherical harmonic. Because of the structure of the Dirac spinor, each basis function of Eq. (8) generates four types of basis spinors,

$$\chi^{L,\alpha}_{p,\rho+}=\begin{bmatrix}\chi_p\\0\\0\\0\end{bmatrix},\quad \chi^{L,\beta}_{p,\rho-}=\begin{bmatrix}0\\\chi_p\\0\\0\end{bmatrix},\quad \chi^{S,\alpha}_{p,\rho+}=\begin{bmatrix}0\\0\\i_{\chi_p}\\0\end{bmatrix},\quad \chi^{S,\beta}_{p,\rho-}=\begin{bmatrix}0\\0\\0\\i_{\chi_p}\end{bmatrix} \tag{9}$$

where ρ is used in place of quantum number $m_\omega=\pm\omega$. ($\rho+=m_p+1/2$ and $\rho-=m_p-1/2$). Each component of the

spinor can be specified by its magnitude and spin. The superscripts $L\alpha$,$L\beta$, $S\alpha$, and $S\beta$ in Eq. (9) refer to spin-up large, spin-down large, spin-up small, and spin-down small components, respectively.[27-29] All the matrix element in F and the resultant C of Eq. (7) become real by the introduction of factor i in the small component. This particular choice for the structure of basis spinors has several computational advantages and lead to an efficient RSCF code as shown in the work of AgH and AuH.[6]

In referring to components of spinors, it is convenient to group them into two; large components and small components. Two large components can be related to the nonrelativistic orbitals or spin orbitals since they can be expressed as a linear combination of nonrelativistic orbitals when the value for the velocity of light is assumed to be infinite. In this view, the small components are auxiliary functions of large components which are necessary to produce relativistic effects and kinetic energy from the relativistic Hamiltonian of Eq. (1). Theoretically, when the velocity of light is assumed to be infinite, the energy of a system from the RSCF calculation should be the same as the nonrelativistic energy obtained in NRSCF calculation using a basis set same as the large component basis set of the RSCF calculation. In practice, this happens only when the large component and small component basis sets are balanced. This is now called "kinetic balance", and the detailed analysis about it is available in the literature.[30] The present RSCF method has been designed to accommodate this condition.

Our calculational methods which yield correct nonrelativistic limits and reasonable relativistic energies for light atoms and diatomic molecules contain, in part, following steps and theoretical considerations.

(1) The large component basis set is constructed from a nonrelativistic basis set for same atoms. Only the integer number n_ρ is considered in STF of Eq. (8). Cusp conditions are not rigorously satisfied in RSCF calculations.[27-29]

(2) The small component basis set is obtained by differentiating all the functions in the large component basis set. Therefore, the small component basis set contains $n=l$ STF's *i.e.*, $1p$, $2d$, $3f$, etc., which are essential for the correct nonrelativistic limit calculations and probably required for reliable RSCF calculations.[21,22]

(3) When the large component basis set is constructed in such a way that many functions with different n and l values share some exponents, much computation time can be saved because same STF's are generated from different STF's for large component space. Although this is purely a computational advantage not affecting the final result, we routinely use basis sets satisfying this condition as shown in Table 1 for Ne. Basis sets satisfying this condition have been generated for many light atoms and some heavy atoms.[31]

(4) The final basis set is a union of the large and small component basis sets. Unique integrals are generated for all STF's in the final set using a modified version of ALCHEMY integral program which is able to handle $n=l$ STF's. A given STF will contribute only to large components or only to small components or to both depending upon derivative condition. In other words, some basis spinors in Eq. (9) generated from a given STF is not included. This procedure generates a complete kinetic balance in the nonrelativistic limit. The number of basis functions contributing in the small component basis set is always larger than that in the large component basis set. This can introduce the error propertional to $1/c^2$ in RSCF calculations but probably has no practical importance for light atoms and molecules.[12,13,15,31]

Table 1. A Single Zeta STF Basis Set[a] for RSCF Calculations of Ne

Exponent	$n\ l$	
	Large component	Small component
9.64200	$1s$	$1p$
2.87923	$2s$, $2p$	$1s$, $2s$, $1p$, $2p$, $2d$

[a] Refers to large component basis set. Small component basis functions are Cartesian derivatives of large component basis functions.

(5) Spinors that belong to negative mass solutions of the Dirac equation are identified in each SCF iteration as those having energy near $-2c^2$ and discarded before the vector selection for the next iteration.

(6) When the derivative condition is used for a basis set selection and thus the kinetic balance is achived, there are no spurious roots[16,32,33] among positive mass (electron) solutions provided that the large component basis set does not contain any $n=l$ STF's Occupied spinors can be selected in each iteration either by spinor energies or by maximum overlap criteria. Both methods have been tested and we have not encountered any convergence problems in RSCF calculations with small basis sets. The omission of STF's with $n=l$ is an additional approximation because the $j=l-1/2$ spiniors of hydrogen-like atoms contains terms which can be best approximated by these $n=l$ STF's.[28,29] When $n=l$ STF's are included in the large component basis set, they produce unphysical spinors of $1p$, $2d$, and $3f$ etc. type whose spinor energies are very close to those of physically meaningful spinors. These unphysical spinors usually cause problems in convergence and we always exclude $n=l$ STF's from the large component basis sets.

In order to show that RSCF calculations performed with the true value for the speed of light ($c=137.036$ a.u.) and those with a very large value of c can be used in the study of relativistic effects for light atoms using basis sets of very small size, we have selected Ne and Kr for our test calculations. Results for these calculations are useful in demonstrating the procedures mentioned above and also provide a critical check of the present RSCF method for diatomic molecules since all the atomic symmetry has to appear in the final answer in order for the program to be correct. Results for H_2 and LiH are also shown in the next section. Although the relativistic effects for these molecules could be interesting, we note that the main emphasis here is to obtain the correct nonrelativistic limit from the RSCF calculations and the sizes of basis sets are kept small for molecular calculations.

Results

Since the derivative of STF functions are the STF with same exponent but with different n or l values,[28] the considerable economy in the number of STF is achieved if the same exponents are used for the same shell as was done

Table 2. Total Energies and Orbital Energies for Ne from RSCF Calculations Using Balanced and Unbalanced Basis Sets Which have 2*s*1*p* and 3*s*3*p*1*d* STF's respectively, in Large Component Basis Sets. Small Component Basis Sets have 3s3p1d STF's in both Cases (All units are in atomic units.)

	$c=137.036$		$c=10^5$	
	Balanced	Unbalanced	Balanced	Unbalanced
$\Gamma_{1/2}$ spinors				
1-11[a]	-3.76×10^4	-3.76×10^4	-2.0×10^{10}	-2.0×10^{10}
1*s*	−32.72	−32.72	−32.66	−32.69
2*s*	−1.740	−1.741	−1.733	−1.735
2*p*	−0.5643	−0.6077	−0.5617	−0.6623
2*p*	−0.5620	−0.5248	−0.5617	−0.5161
spurious[b]		−91.97,		−92.01,
		−30.53,		−30.53,
		−6.26, , , ,		−6.24,
$\Gamma_{3/2}$ spinors				
1-5[a]	-3.76×10^4	-3.76×10^4	-2.0×10^{10}	-2.0×10^{10}
2*s*	−0.5620	−0.5248	−0.5617	−0.5161
spurious[b]		−91.97,		−92.01,
		−6.26, , , ,		−6.24, , , ,
E_T	−127.9492	−127.9242	−127.8122	−127.7856
ΔE_R $[E_T(c=c)-E_T(c=10^5)]$			−0.1370	−0.1386

[a] Negative mass solutions, [b] Only those with negative spinor energies are given.

in some nonrelativistic case.[34] With this prescription, the single zeta basis set is generated for Ne, as shown in Table 1. Since small component basis sets are automatically generated from the corresponding large component basis set, only the large component basis sets are referred as single zeta, double zeta etc. The single zeta basis set for Ne has one STF for each occupied shell (2-*s*, 1-*p*) and small components are the Cartesian derivatives of large component. Eigenvalues obtained in the SCF iteration are shown in Table 2 for different c values and the large component basis set. The balanced basis set contains only (2-*s*, 1-*p*) STF in the large component space. The unbalanced basis set is constructed by allowing all the small component basis set to act also as the large component basis set. Thus some of the derivative functions of the large components are missing from the small component space and the kinetic balance is broken even for $c=10^5$ a.u.

These were no difficulties in identifying the negative mass solution for any cases since all the negative mass solutions have eigenvalues near $-c^2$ (Table 2). Therefore it is possible to eliminate negative mass solutions just by examining the eigenvalues. Discarding the negative mass solution is equivalent to project out only the positive mass solutions with an approximate projection operator. This projection operator is only approximate since the exact solution is not known until the convergence. We have not experience any ambiguities in eliminating the negative mass solutions even for the system as heavy as Au.

The unbalanced basis set has spurious eigenvalues interleaved with meaningful ones as shown in Table 2. Even for the unbalanced basis set, it is possible to converge in some cases by selecting the eigenvectors by maximum overlap with the good initial guess. However, the SCF procedure may not converge in many cases since most systems are more complicated than Ne single zeta calculations. The Ne calculation with unbalanced basis set converge to energies about 0.02 a.u. lower than the balanced basis set energies for both $c=137.036$ (true value for speed of light) and $c=10^5$ (nonrelativistic case), producing the relativistic contribution to the total energy of −0.1386 a.u. compared with −0.1370 a.u. for the balanced one. The eigenvalues, however, display nonphysical behavior, *i.e.*, split 2*p* orbitals for $c=10^5$ in addition to the appearance of spurious roots. It appears that some of previous RSCF calculations of other workers suffer from deficiencies in basis sets.[23,19]

Table 3. Total Energies of Ne (in a.u.) from larious calculations

Basis set	Large comp.	Small comp.	Method[a]	$-E_T$	$-\Delta E_R$
SZ	2*s*1*p*	4*s*2*p*1*d*	RSCF(137.036)	127.94923	
			RSCF(10^5)	127.81218	0.1371
	2*s*1*p*		NRSCF[b]	127.81218	
DZF	4*s*2*p*	6*s*6*p*2*p*	RSCF(137.036)	128.56001	
			RSCF(10^5)	128.41783	0.1422
	4*s*2*p*		NRSCF[b]	128.41783	
Extended	6*s*4*p*	10*s*10*p*4*d*	RSCF(137.036)	128.69175	
			RSCF(10^5)	128.54702	0.1447
Extended	6*s*4*p*	10*s*6*p*4*d*	RSCF(137.036)	128.69188	
			RSCF(10^5)	128.54706	0.1448
Numerical			DHF(137.036)[c]	128.69197	
			NRHF[d]	128.547	0.145
Extended			RSCF(137.036)[e]	128.6919	
			NRSCF[f]	128.54705	0.145

[a] Values in parenthesis refer to different values of c(in a.u.) used in relativistic calculations. [b] Nonrelativistic SCF calculations. [c] Atomic DHF calculations. [d] Nonrelativistic numerical HF calculations. [e] Atomic DHF calculations of Ref. 21. [f] Atomic HF calculations.

The RSCF calculation with sufficiently large value of c using balanced basis set, which contain all the derivatives of the large component basis functions in the small component basis set, always yield the same energy as the NRSCF calculation for which the basis set is identifical to the large component basis set of RSCF calculation as shown in the several basis calculations of Ne in Table 3. This eliminates the ambiguity in defining relativistic effects. Relativistic contributions estimated from RSCF calculations approach that from the HF and DHF calculations as the basis set for the large component increase from singl-zeta to extended (6*s*, 4*p*). The estimate of the relativistic effect is already reasonable, being less than 10% error, even in the single-zeta calculation as shown in Table 3.

In the extended basis set calculations, the small component space is highly crowded. It is appearent that the linear dependency of the basis functions will become the major problems in the large calculations if the kinetic balance is achieved by adding derivatives of all the large component

Table 4. Total Energies for Kr from RSCF and DHF Calculations

	c	E_T	$-\Delta E_R$
RSCF[a]	137.036	−2772.38509	
	10^5	−2738.08150	
	10^6	−2738.08143	
	10^7	−2738.08143	34.304
DHF[b]	137.036	−2788.885	36.825

[a]Present RSCF calculations with the single zeta STF basis set (*4s3p1d* for large component and *7s7p5d1f* for samll component space). [b]Numerical DHF calculation.

basis functions into the small component basis set as in our calculations. In order to avoid the possible linear dependency as well as to economize the calculation, we have omitted some of derivative functions from the small component space in the extened basis set calculations of Ne. This omission lowers the total energies of Ne by 0.0001 a.u. for $c=137.036$ and 0.00004 a.u. for $c=10^5$, when the energies using *10s6p4d* small component basis set are compared with those using *10s10p4d*. For many practical purposes, one may be able to omit some of derivative functions of large systems without sacrificing too much accuracy in the result. When the derivative conditions are reasonably satisfied, the spurious eigenvalues do not appear. We have used these qualitatively correct small component basis set in our studies of the large systems.[6,31] The actural selection of small component basis set may depend on the problems at hand since the full deriviative small components, while large in size, eliminate the necessity to perform $c=10^5$ calculations.

Another test calculations with a single zeta basis set are done for Kr (Table 4). The total energies of Kr are calculated at several value of c and the total energy at $c=10^7$ is the same as the total energy from NRSCF calculation with the large component basis set. The large value $c=10^6$ is required for Kr than for Ne where $c=10^5$ is sufficient, in order to obtain nonrelativistic energy coffect to 10^{-4} a.u. in the RSCF calculation. The error in the nonrelativistic energy is roughly proportional to Z^2/c^2 or to the total energy divided by c^2, thus large values are needed for the nonrelativistic limit calculations as the atomic number increases. The nonrelativistic energy with $c=10^5$ is still acceptable for this system. Since we will be mainly interested in the molecular properties, we think that $c=10^5$ is a practical compromise for properties defined by the differences among various atomic arrangement. The relativistic contributions to the total energy estimated in this single zeta RSCF calculations, −34.3 a.u., is again within 10% of the limiting value, −36.8 a.u. from DHF calculations.

The LiH molecule at $R=3.015$ a.u. is calculated using 6*s* (4*s* on Li and 2*s* on H) large component basis set and two different small component basis sets, and the results are summarized in Table 5. The large component basis set is the same as that of Matsuoka, Suzuki, Aoyama and Malli (MSAM).[23] One small component basis set, which is denoted as 6*p*(S) in Table 5, is similar to that used by MSAM except that MSAM used basis spinors with two non-zero components whereas ours have only one non-zero component as in Eq. (9). The other denoted as 8*p*(S) contains all the derivatives of the large component basis functions. The latter bais set contains two more 1*p* functions which have the same exponents as the 2*s* large component STF's and satisfies the kinetic balance. Results of our RSCF calculations with 6*p*(S) basis set agree reasonable well with those of MSAM. Small differences of 10^{-6} a.u. in total energies and 10^{-4} a.u. in orbital energies might be due to the different accuracies in numerical procedures and/or additional basis set effects explanined later. The energies of 6*p*(S) basis set and MSAM differ from that from NRSCF calculations by 3×10^{-5} a.u., which disappears for 8*p*(S) basis set. The relativistic effects are, however, the same for both basis sets within the numerical accuracy of the calculations. It is interesting that the unbalanced basis set, 6*p*(S), yields energy lower than the balanced basis set 8*p*(S) in Table 5.

Table 5. Total Energies (E_T) and Orbtial Energies (ε_i) of LiH (in a.u.) from RSCF Calculations at $R=3.015$ a.u.

Basis[a]		Balanced 6*s*(L)-8*p*(S)	Unbalanced 6*s*(L)-6*p*(S)	Unbalanced MSAM[b]
RSCF	E_T	−7.970574	−7.970602	−7.970604
($c=137.036$)	ε_1	−2.471923	−2.471775	−2.47171
	ε_2	−0.298305	−0.298332	−0.29833
RSCF[c]	E_T	−7.969756	−7.969784	−7.969785
($c=10^5$)	ε_1	−2.471726	−2.471559	−2.47098
	ε_2	−0.298310	−0.298319	−0.29869
$-\Delta E_R$		0.000818	0.000818	0.000818

[a]L and S in parantheses refer to large and small component basis sets, respectively. [b]Results of Matsuoka, Suzuki, Aoyama and Malli in Ref. 23. [c]Results from NRSCF calculation using 6*s* STF basis set are the same as those from RSCF with $c=10^5$ using balanced basis set for all figures reported.

The total energies calculated in RSCF calculations using unbalanced basis sets are lower than those using balanced basis sets due to the underestimate of kinetic energies.[6,12-16] These effects of incomplete small basis sets are evident in many calculations.[6,23,19] However, when the number of functions in the small component basis is far greater than that in the large component, this extra small-component basis functions can raise energy in the order of c^{-4} in one-electron atoms and probably cause larger errors in many-electron system.[31] Since this effects is not readily observed in our present calculations, we assume that our basis sets are correctly balanced. If MASM's and 6*p*(S) LiH calculations have exactly the same computational accuracy, the small differences between two results could be due to different partitioning of small component basis functions. Matsuoka showed the equivalence of their "unified basis spinors" (UBS) and our "separated basis spinors", (SBS),[35] although their UBS correspond to "restricted kinetic balance" (RKB) while our SBS correspond to "unrestricted kinetic balance" (UKB).[36] Actual calculations with UKB always give higher total energy than those with RKB,[36] because larger degree of freedom in small component space produces higher total energy as a result of nonvariational characteristics of the relativistic calculations. Such dependence of the energy on the degree of freedom in the small component space was noted earlier in our previous work.[37] All calculations in the present paper with

Table 6. Basis set for H_2 Calculations

Exponents	*n l*	
	Large	Small
2.91039	1*s*	1*p*
1.45363	1*s*	1*p*
1.00	1*s*, 2*s*, 2*p*	1*s*, 2*s*, 1*p*, 2*p*, 2*d*

Table 7. Total (E_T), Electronic (E_e), and Orbital (ε) Energies for H_2 from RSCF Calculations using a 4*s*1*p*(L)-4*s*4*p*1*d*(S) STF basis Set.[a] Only Relativistic Energies (in a.u.) are Given in This Table

R^b	$-E_T$	$-E_e$	$-\Delta E_R(\times 10^{-5})^c$	$-\varepsilon$	$-\Delta\varepsilon(\times 10^{-6})^d$
0.0(He)		2.8618091	13.31	0.9179847	34.0
0.5	0.4851698	2.4851698	4.91	0.7979123	12.5
1.0	1.0831024	2.0831024	2.12	0.6699751	5.8
1.38	1.1320949	1.8567326	1.41	0.5981961	4.0
1.39	1.1321130	1.8515374	1.40	0.5965511	4.0
1.40	1.1320914	1.8463771	1.39	0.5949173	4.0
∞(2 H)		1.0000130	1.30	0.5000067	6.7

[a] A double zeta basis set for He is contained in this basis set. [b] Internuclear distances. [c] $\Delta E_R = E_e\ (c=137.036) - E_e(c=10^5)$. The values from the nonrelativistic calculations are the same as those from RSCF calculations with $c=10^5$ upon all the figures reported. [d] $\Delta\varepsilon = \varepsilon(c=136.036) - \varepsilon(c=10^5)$.

UKB show no intruder states,[36] once $n=l$ functions are not allowed in the large component space.

The potential curve of the H_2 is calculated using the 4*s*1*p* large component basis set of Table 6 on each hydrogen. This basis set is double zeta plus polarization quality with He basis included for the comparable calculations in the united atom limit. The number of STF's are reduced by using the same exponents for different *n* and *l* functions.[31] The relativistic effects in the total energies of H_2 are very small (10^{-5} a.u.) as expected and increase as two H atom approach each other reaching maximum in the united atom (He) limit as shown in Table 7. The relativistic correction of 6.65×10^{-5} a.u. for the total energy of He shown in Table 7 agrees exactly with the numerical DHF value[28] as one might have expected from Ne calculations discussed earlier. The relativistic effect in the total energy of 1.4×10^{-5} a.u. (3.8×10^{-4} eV) at the equilibrium bond length can be compared with the converged value obtained by MSAM[38] with GTO basis sets. Results in Table 7, therefore, may be considered as the basis set limit values in the SCF level as far as the relativistic corrections are concerned.

Since relativistic effects increase monotonically as R decreases, we expect that relativistic effects on H_2 shorten the bond length and slightly increase the dissociation energy in the SCF calculations. This may be a general phenomenon in diatomic molecules with covalent bond mainly composed of *s* selectrons as shown in heavier systems like AuH, AgH,[6] and Au_2,[39] calculated with RSCF or effective core potential methods. Orbital energies are affected less by the relativity than the total energies. The relativistic effects on orbital energies have a minimum near equilibrium bond length as shown in Table 7. This is probably due to the fact that the small components have antibonding combinations.

Summary and Discussion

There are three major difficulties associated with RSCF calculations. These are the definition of the relativistic energy, convergences in the RSCF procedure and the size of the calculation. All these problems are caused by the existence of negative mass solutions and small components. In this paper, we have aimed at presenting practical solutions for the correct definition of the relativistic energy and for avoiding the convergence problems with main emphasis on computational illustrations rather than on theoretical analyses for which many excellent discussions are available in the literature.[12-16] Both problems are solved by utilizing a kinetically balanced basis set, which we obtain by including all the derivatives of the large component basis functions in the small component basis set. We do not use $n=l$ STF's in the large component basis set.

We have not considered computational efficiency which is also crucial for successful applications of the RSCF method. The present RSCF method is efficient enough to handle diatomic molecules of moderate size as demonstrated by actual calculations,[6,40] but further optimizations of the computational methods are worthwhile in order to make RSCF calculations as routine as NRSCF ones. Selection of large component basis sets for heavy atoms and reducing the size of corresponding small component basis sets are also necessary steps. We are currently working on these problems and some results are available elsewhere.[31] Extensions to many directions[24] seem to be not only interesting but also reasonable considering the success of DHF method for atoms and considering the ever increasing computational powers. Relativistic electronic structure calculations are still at the beginning state, but most methods developed for nonrelativistic treatments could be adopted in relativistic calculations once the nature of spinors is reasonably understood.

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Novel Polysilamethylenosilanes; New Precursors for Silicon Carbide

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Novel polysilamethylenosilanes (PSMS) were prepared by Wurtz type co-condensation of various mixtures of 2,4,4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane (TSH) and dimethyldichlorosilane (D). When TSH was incorporated more than 25 mole%, PSMS polymers were soluble in common organic solvents probably due to the polycarbosilane linkage brought from TSH. The molecular weights of the polymer were measured by gel permeation chromatography and showed higher molecular weight with high TSH content. The thermal gravimetric residues increased as TSH contents increased. These properties suggested that PSMS polymers could be useful as ceramic precursors for silicon carbide.

Introduction

The polysilane processing route to silicon carbide has received an exploratory research interest in industry and in academic sector[1] as well since Yajima *et al.* reported the utilization of dimethylpolysilane as the silicon carbide pre-