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Dirac–Fock–Roothaan calculations using a relativistic reduced frozen-core approximation

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The reduced frozen-core approximation (RFCA) that has been previously used for nonrelativistic calculations is extended to relativistic calculations. The RFCA adopts a new method for the orthogonalization of valence basis functions to core orbitals. Orthogonalization is performed using *corelike* basis functions consisting of fewer primitive basis functions than *core* orbitals. Dirac–Fock–Roothaan calculations on HI and ThO show that the relativistic RFCA can reduce computing time and closely reproduce the total and valence orbital energies and spectroscopic constants obtained by all-electron calculations. © *1998 American Institute of Physics.* [S0021-9606(98)30443-2]

I. INTRODUCTION

Despite rapid progress in computer technologies, all-electron (AE) Dirac–Fock–Roothaan (DFR) calculations on molecules containing heavy atoms still require considerable computer time. To reduce the computational requirements, the frozen-core approximation (FCA) could be adopted, since the FCA treats a few valence electrons explicitly and leaves core electrons dormant.

For example, population analysis on our previous AE DFR calculations on ThO molecule[1] shows that the lower orbitals of ThO consist of the core orbitals of the constituent atoms and only the $5d$, $6p$, and $7s$ orbitals of the thorium atom and the $2s$ and $2p$ orbitals of the oxygen atom take part in molecule formation. Thus, the FCA should work very well in heavy-atom containing molecules, as assumed in many model and pseudopotential calculations.[2]

In the usual FCA, the valence basis functions $\{\chi_p\}$ are Schmidt orthogonalized to core orbitals $\{\phi_c\}$ to form core-orthogonalized valence basis functions $\{\omega_p\}$ as

$$\omega_p = N_p\left(\chi_p - \sum_c \phi_c C_{cp}\right), \tag{1}$$

where N_p is a normalization constant and $\{C_{cp}\}$ are coefficients to be determined so that $\langle\omega_p|\phi_c\rangle = 0$. Hence, to perform DFR calculations, molecular integrals over basis functions $\{\chi_p, \phi_c\}$ are needed, so that the usual FCA requires the same number of molecular integrals as AE calculations. Thus, with regard to the computation of molecular integrals, the former approach does not have much merit over the latter.

To overcome this drawback, one of the authors[3] proposed a new kind of FCA called reduced FCA (RFCA). In RFCA, each core orbital ϕ_c has a one-to-one correspondence to a *corelike* basis function κ_c, and the valence basis functions are orthogonalized to core orbitals through corelike basis functions $\{\kappa_c\}$ as

$$\omega_p = N_p\left(\chi_p - \sum_c \kappa_c C_{cp}\right), \tag{2}$$

such that $\langle\omega_p|\phi_c\rangle = 0$. Several numerical calculations have shown that the corelike basis function κ_c can be selected so that the basis is simpler and smaller than that of the corresponding core orbital ϕ_c. Hence, the required molecular integrals are over the basis set $\{\chi_p, \kappa_c\}$, and the computation of molecular integrals should be simplified compared to AE calculations.

This scheme of selecting corelike basis functions is similar to the one adopted by the model and some of the effective core-potential methods.[2] Hence the proposed RFCA could be regarded as rigorism of these approximate methods[2] as noted in the previous article.[3]

In the previous article,[3] *nonrelativistic* Hartree–Fock–Roothaan calculations were performed using RFCA and the calculated total and orbital energies and spectroscopic constants were found to be comparable to those obtained by AE calculations. In this article, RFCA is extended to *relativistic* Hartree–Fock–Roothaan (or DFR) calculations.

The relativistic RFCA is described in Sec. II, and numerical calculations for HI and ThO using the relativistic RFCA are reported in Sec. III. The proposed relativistic RFCA is discussed in Sec. IV. Throughout this article, atomic units will be used except when noted otherwise.

II. RELATIVISTIC REDUCED FROZEN-CORE APPROXIMATION

A. Relativistic Hamiltonian

The relativistic RFCA does not differ much from the nonrelativistic RFCA.[3] The valence basis function χ_p is orthogonalized to core orbitals ϕ_c through corelike basis functions κ_c as in Eq. (2). However, they consist of four components, and the Dirac–Coulomb Hamiltonian is assumed so that the core Hamiltonian for electron μ is written as

$$H^{\text{core}}(\mu) = H_D(\mu) + \sum_I V_I^{\text{core}}(\mu), \tag{3}$$

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TABLE I. Basis functions for 5*s* valence orbital of iodine atom.

Primitive bases η	Exponent parameters	Coefficients		Corelike or valence bases
		Large comp.	Small comp.	
1	2.8915*E*+7	2.1402*E*−6	4.4822*E*−6	1*s* corelike
2	5.1083*E*+6	6.0271*E*−6	1.3719*E*−5	
3	1.3702*E*+6	1.4829*E*−5	2.9116*E*−5	
4	4.2138*E*+5	3.9439*E*−5	6.5273*E*−5	
5	1.3372*E*+5	1.1214*E*−4	1.4273*E*−4	
6	4.4116*E*+4	3.2593*E*−4	2.9985*E*−4	
7	1.5337*E*+4	9.2548*E*−4	5.8343*E*−4	
8	5.7406*E*+3	2.4267*E*−3	1.0291*E*−3	
9	2.3397*E*+3	5.5409*E*−3	1.5859*E*−3	
10	1.0250*E*+3	1.0914*E*−2	2.1386*E*−3	
11	4.7447*E*+2	1.5343*E*−2	2.0896*E*−3	
12	2.2772*E*+2	8.1254*E*−3	7.9068*E*−4	
13	1.1091*E*+2	−3.9525*E*−2	−2.6009*E*−3	2*s* corelike
14	5.4635*E*+1	−1.0582*E*−1	−4.9320*E*−3	
15	2.6961*E*+1	−5.6286*E*−2	−1.8538*E*−3	
16	1.3428*E*+1	2.5199*E*−1	5.8282*E*−3	3*s* corelike
17	6.7745*E*+0	3.1805*E*−1	5.2326*E*−3	
18	3.3211*E*+0	−2.6691*E*−1	−3.0726*E*−3	4*s* corelike
19	1.6286*E*+0	−6.3852*E*−1	−5.1495*E*−3	
20	8.1634*E*−1	−1.6800*E*−1	−9.5938*E*−4	
21	3.7650*E*−1	5.6692*E*−1	2.1984*E*−3	5*s* valence
22	1.9181*E*−1	5.4053*E*−1	1.4961*E*−3	
23	9.6515*E*−2	2.3022*E*−1	4.5200*E*−4	

where the first term is the mass-energy-subtracted Dirac Hamiltonian[4]

$$H_D(\mu)=c\,\boldsymbol{\alpha}\cdot\mathbf{p}+c^2\boldsymbol{\beta}'+\sum_I \nu_I(\mu) \tag{4}$$

and the second term consists of Coulomb (*J*) and exchange (*K*) potentials[4] from core electrons at the *I*th nucleus:

$$V_I^{\mathrm{core}}(\mu)=\sum_{c\subset I}[J_c^I(\mu)-K_c^I(\mu)]. \tag{5}$$

In Eq. (4), c is the speed of light, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}'$ are Dirac matrices, $\mathbf{p}=-i\boldsymbol{\nabla}$ is the momentum operator, and $\nu_I(\mu)$ is the nuclear potential from the *I*th nucleus. In this study, nuclei are assumed to be uniformly charged spheres.[5]

B. Valence basis functions

After some numerical calculations, we found that we could safely treat the four-component valence basis functions as units so that we could expand the four-component molecular orbitals ϕ_i in terms of core-orthogonalized valence basis functions $\{\omega_p\}$ as

$$\phi_i=\sum_p \omega_p C_{pi} \tag{6}$$

and the scalar coefficients $\{C_{pi}\}$ were optimized by the self-consistent field (SCF) process. This is in contrast to usual AE calculations where the coefficients on the large and small components are optimized individually. (See e.g., Ref. 6).

The large and small components of the valence basis functions χ_p are taken atomic balanced,[7,8] where the primitive basis functions are taken kinetic balanced.[9] The large and small components of the polarization functions, η_p^L and η_p^S, were found to be safely taken kinetic balanced[9] as

$$\eta_p^S=\sigma\cdot\mathbf{p}\,\eta_p^L/2c, \tag{7}$$

where σ is a Pauli matrix.

TABLE II. Square norms of large (ϕ^L) and small (ϕ^S) components for thorium atomic orbitals.

Orbital	Orb. energy	$\langle\phi^L\vert\phi^L\rangle$	$\langle\phi^S\vert\phi^S\rangle$	$\langle\phi^S\vert\phi^S\rangle/\langle\phi^L\vert\phi^L\rangle$
1*s*+	−4058.5	0.87907	1.2093*E*−01	1.3757*E*−01
2*s*+	−758.57	0.97160	2.8399*E*−02	2.9229*E*−02
2*p*−	−729.88	0.97151	2.8494*E*−02	2.9330*E*−02
2*p*+	−603.59	0.97568	2.4319*E*−02	2.4925*E*−02
3*s*+	−193.11	0.99027	9.7325*E*−03	9.8282*E*−03
3*p*−	−180.13	0.99033	9.6720*E*−03	9.7665*E*−03
3*p*+	−150.89	0.99154	8.4637*E*−03	8.5360*E*−03
3*d*−	−130.31	0.99168	8.3182*E*−03	8.3880*E*−03
3*d*+	−124.36	0.99199	8.0078*E*−03	8.0724*E*−03
4*s*+	−50.195	0.99653	3.4725*E*−03	3.4846*E*−03
4*p*−	−44.347	0.99663	3.3725*E*−03	3.3839*E*−03
4*p*+	−36.715	0.99706	2.9416*E*−03	2.9502*E*−03
4*d*−	−27.325	0.99728	2.7230*E*−03	2.7305*E*−03
4*d*+	−25.902	0.99739	2.6090*E*−03	2.6158*E*−03
4*f*−	−13.535	0.99775	2.2457*E*−03	2.2507*E*−03
4*f*+	−13.177	0.99780	2.1989*E*−03	2.2037*E*−03
5*s*+	−11.568	0.99895	1.0501*E*−03	1.0512*E*−03
5*p*−	−9.2495	0.99904	9.6412*E*−04	9.6505*E*−04
5*p*+	−7.5061	0.99918	8.2382*E*−04	8.2449*E*−04
5*d*−	−3.9814	0.99936	6.4372*E*−04	6.4414*E*−04
5*d*+	−3.7186	0.99939	6.0917*E*−04	6.0954*E*−04
6*s*+	−2.0658	0.99975	2.5201*E*−04	2.5208*E*−04
6*p*−	−1.3172	0.99979	2.0581*E*−04	2.0585*E*−04
6*p*+	−1.0017	0.99984	1.6256*E*−04	1.6258*E*−04
6*d*−	−0.22275	0.99993	6.6740*E*−05	6.6744*E*−05
6*d*+	−0.21044	0.99994	6.0611*E*−05	6.0615*E*−05
7*s*+	−0.20933	0.99997	3.1934*E*−05	3.1935*E*−05

C. Corelike basis functions

After several numerical experiments, we found that the following procedure gave an appropriate set of corelike basis functions $\{\kappa_c\}$. First, we perform AE atomic DFR calculations using a given set of primitive basis functions. The Dirac–Fock valence orbitals usually consist of groups of basis functions such that the primitive basis functions in each group have coefficients with the same signs. Table I shows as an example the 5*s* valence orbital of iodine atom calculated using exponent parameters of a well-tempered basis set.[10] It consists of five groups of basis functions: ($\eta_1-\eta_{12}$), ($\eta_{13}-\eta_{15}$), (η_{16},η_{17}), ($\eta_{18}-\eta_{20}$), and ($\eta_{21}-\eta_{23}$). We take the first group ($\eta_1-\eta_{12}$) to be a 1*s* corelike basis function κ_{1s}, the second group ($\eta_{13}-\eta_{15}$) is a 2*s* corelike basis function κ_{2s} etc., and the fifth group ($\eta_{21}-\eta_{23}$) is the valence basis functions. For other atoms, we can use the same procedure as in this example. Second, we apply least-square fitting to these corelike basis functions κ_{1s} etc. using fewer primitive basis functions. Next, we perform DFR calculations using these corelike and valence basis functions and see whether they give reasonable total and orbital energies. If so, we consider them to be an appropriate set of basis functions to be adopted for molecular RFCA calculations.

TABLE III. Basis-set contractions shown as ''number of primitive functions/sizes of contractions.'' Corelike basis functions are underlined and polarization functions are marked by asterisks.

		AE	RFCA1	RFCA2	RFCA3
H	$s+$	$5/3,1^2$	$5/1^5$	$5/1^5$	$5/1^5$
	$p-,p+$	1/1*	1/1*	1/1*	1/1*
O	$s+$	$10/4,1^6$	$10/\underline{5},1^5$	$9/\underline{4},1^5$	$8/\underline{3},1^5$
	$p-,p+$	$6/3,1^3$	$6/3,1^3$	$6/3,1^3$	$6/3,1^3$
	$d-,d+$	1/1*	1/1*	1/1*	1/1*
I	$s+$	$23/4,2,1^{17}$	$21/\underline{10},\underline{3},\underline{2},\underline{3},1^3$	$18/\underline{7},\underline{3},\underline{2},\underline{3},1^3$	$16/\underline{5},\underline{3},\underline{2},\underline{3},1^3$
	$p-$	$21/5,1^{16}$	$19/\underline{9},\underline{3},\underline{2},1^5$	$16/\underline{6},\underline{3},\underline{2},1^5$	$14/\underline{4},\underline{3},\underline{2},1^5$
	$p+$	$21/5,1^{16}$	$18/\underline{8},\underline{3},\underline{2},1^5$	$15/\underline{5},\underline{3},\underline{2},1^5$	$13/\underline{3},\underline{3},\underline{2},1^5$
	$d-,d+$	$15/3,2,1^8,1^{*2}$	$14/\underline{7},1^5,1^{*2}$	$12/\underline{5},1^5,1^{*2}$	$11/\underline{4},1^5,1^{*2}$
Th	$s+$	$24/5,2,1^{17}$	$24/\underline{11},\underline{2},\underline{2},\underline{2},\underline{2},\underline{2},1^3$	$19/\underline{6},\underline{2},\underline{2},\underline{2},\underline{2},\underline{2},1^3$	$17/\underline{4},\underline{2},\underline{2},\underline{2},\underline{2},\underline{2},1^3$
	$p-$	$20/6,1^{13},1^*$	$20/\underline{10},\underline{2},\underline{2},\underline{2},1^3,1^*$	$16/\underline{6},\underline{2},\underline{2},\underline{2},1^3,1^*$	$16/\underline{6},\underline{2},\underline{2},\underline{2},1^3,1^*$
	$p+$	$20/6,1^{13},1^*$	$20/\underline{10},\underline{2},\underline{2},\underline{2},1^3,1^*$	$14/\underline{4},\underline{2},\underline{2},\underline{2},1^3,1^*$	$14/\underline{4},\underline{2},\underline{2},\underline{2},1^3,1^*$
	$d-$	$16/3,3,1^{10}$	$16/\underline{7},\underline{2},\underline{3},1^4$	$13/\underline{4},\underline{2},\underline{3},1^4$	$12/\underline{3},\underline{2},\underline{3},1^4$
	$d+$	$16/3,3,1^{10}$	$16/\underline{7},\underline{2},\underline{3},1^4$	$13/\underline{4},\underline{2},\underline{3},1^4$	$11/\underline{2},\underline{2},\underline{3},1^4$
	$f-,f+$	$12/8,1^{*4}$	$12/\underline{8},1^{*4}$	$9/\underline{5},1^{*4}$	$9/\underline{5},1^{*4}$

D. Size of the small components of valence basis functions

In some AE DFR calculations,[11,12] two-electron integrals involving only small-component basis functions χ^S, $(\chi^S\chi^S|\chi^S\chi^S)=(SS|SS)$, have been neglected completely by assuming that they should contribute very little to the total energy, etc., compared to those involving large-component basis functions χ^L, $(\chi^L\chi^L|\chi^L\chi^L)$ and those involving both components, $(\chi^L\chi^L|\chi^S\chi^S)$. This should lead to an enormous reduction in computing time for two-electron integrals. However, this supposition does not hold for integrals involving core basis functions. Table II shows, with thorium atom as an example, the square norms of large-component ϕ^L, $\langle\phi^L|\phi^L\rangle$, small-component ϕ^S, $\langle\phi^S|\phi^S\rangle$, and their ratios $\langle\phi^S|\phi^S\rangle/\langle\phi^L|\phi^L\rangle$. As shown, the ratios for the core orbitals are fairly large, while those for the valence orbitals are smaller. This suggests that we can neglect $(SS|SS)$ integrals involving only valence basis functions $\{\omega_p\}$ in Eqs. (2) and (6). This approximation will be shown to work very well numerically in the next section.

We should note that other schemes[13–17] were also proposed for neglecting $(SS|SS)$ integrals.

E. Calculation of matrix elements for core Hamiltonian

Even if we adopted the proposed RFCA and could reduce the computing time for two-electron integrals over the valence basis functions $\{\omega_p\}=\{\chi_p,\kappa_c\}$, we need the matrix elements of the core Hamiltonians defined by Eqs. (3)–(5). These need at most three-center two-electron integrals involving the core and valence basis functions $\{\phi_c,\chi_p\}$ and require considerable computing time. To reduce the computing time required, we adopted the spectral representation technique as used in the nonrelativistic RFCA[3] as well as the model and pseudopotential calculations[2] and rewrote the potentials arising from the Ith core as

$$\nu_I(\mu)+V_I^{\mathrm{core}}(\mu)=\nu(Z_I-Z_I^{\mathrm{core}})+\Omega^I[\,\nu(Z_I^{\mathrm{core}})+V_I^{\mathrm{core}}(\mu)\,]\Omega^I. \tag{8}$$

TABLE IV. Total energies (E) and valence orbital energies (ϵ) of basis sets of Table II.

		AE	RFCA1	RFCA2	RFCA3
H	$\epsilon(1s+)$	−0.499 82	−0.499 82	−0.499 82	−0.499 82
O	E	−74.820 08	−74.820 08	−74.819 63	−74.817 16
	$\epsilon(2s+)$	−1.250 94	−1.250 94	−1.250 72	−1.249 52
	$\epsilon(2p-)$	−0.615 64	−0.615 63	−0.615 68	−0.615 93
	$\epsilon(2p+)$	−0.614 22	−0.614 22	−0.614 26	−0.614 52
I	E	−7115.793 08	−7115.793 06	−7115.789 72	−7115.761 33
	$\epsilon(5s+)$	−0.876 76	−0.876 75	−0.876 71	−0.877 26
	$\epsilon(5p-)$	−0.430 57	−0.430 57	−0.430 51	−0.430 61
	$\epsilon(5p+)$	−0.388 72	−0.388 72	−0.388 72	−0.387 68
	$\epsilon(4d-)$	−2.342 40	−2.342 40	−2.342 38	−2.344 88
	$\epsilon(4d+)$	−2.275 11	−2.275 11	−2.275 22	−2.278 18
Th	E	−26510.561 12	−26510.563 34	−26510.554 45	−26510.542 11
	$\epsilon(7s+)$	−0.209 33	−0.209 33	−0.209 26	−0.209 11
	$\epsilon(6p-)$	−1.317 21	−1.317 20	−1.315 28	−1.320 84
	$\epsilon(6p+)$	−1.001 63	−1.001 63	−1.001 51	−1.006 20
	$\epsilon(6d-)$	−0.222 69	−0.222 71	−0.222 76	−0.223 55
	$\epsilon(6d+)$	−0.210 40	−0.210 41	−0.210 52	−0.205 40

TABLE V. Total energies (E) and valence orbital energies (ϵ) for HI at internuclear distance of 3.00 a.u.

	$-E$	$-\epsilon(15e_{1/2})$	$-\epsilon(16e_{1/2})$	$-\epsilon(17e_{1/2})$	$-\epsilon(8e_{3/2})$
AE	7116.379 55	0.919 65	0.538 59	0.399 75	0.372 61
RFCA1	7116.379 47	0.919 73	0.538 63	0.399 73	0.372 58
RFCA1*[a]	7116.379 50	0.919 73	0.538 63	0.399 73	0.372 58
RFCA1s[b]	7116.379 50	0.919 73	0.538 63	0.399 72	0.372 57
RFCA2	7116.376 13	0.919 70	0.538 61	0.399 69	0.372 58
RFCA2*[a]	7116.376 15	0.919 70	0.538 61	0.399 69	0.372 58
RFCA2s[b]	7116.376 00	0.919 69	0.538 62	0.399 68	0.372 58
RFCA3	7116.347 58	0.920 18	0.538 51	0.399 42	0.371 59
RFCA3*[a]	7116.347 61	0.920 18	0.538 51	0.399 42	0.371 59
RFCA3s[b]	7116.347 36	0.920 21	0.538 52	0.399 42	0.371 56

[a]RFCA calculation without $(SS|SS)$ integrals over valence basis functions.
[b]RFCA calculation using spectral representations for core Hamiltonians.

The nuclear potential from the Ith nucleus of nuclear charge Z_I on the left hand side (lhs), $\nu_I(\mu)\equiv\nu(Z_I)$, has been decomposed to those on the right hand side (rhs) and the potential from the Z_I^{core} core electrons has been sandwiched by the spectral operators on the Ith nucleus:

$$\Omega^I=\sum_{p,q\subset I}|p\rangle(\mathbf{S}^{-1})_{pq}\langle q|, \tag{9}$$

where $\mathbf{S}^{-1}$ is an inverse of the overlap matrix $\mathbf{S}$ whose (p,q) element $S_{pq}=\langle p|q\rangle$ is an overlap integral over spectral functions $|p\rangle$ and $|q\rangle$. If we evaluate the matrix elements over the operators on the rhs of Eq. (8), then we do not need to calculate two- and three-center two-electron integrals and could reduce the computing time required to calculate the matrix elements of core Hamiltonians. This approximation will be examined numerically in Sec. III.

III. NUMERICAL CALCULATIONS

We performed DFR calculations on several molecules to test the relativistic RFCA described above. We report here the details of the results for HI and ThO.

A. Basis sets

We took the exponent parameters of iodine from the atomic DFR Gaussian basis set of Okada and Matsuoka,[18] which were originally from the well-tempered Gaussian basis set of Huzinaga and Klobukowski,[10] and those of hydrogen from Yamamoto and Matsuoka.[19] Two d-type Gaussian functions of iodine with exponents of 0.096 515 30 and 0.191 805 34[18] were augmented as polarization functions, and a p-type function of hydrogen with an exponent of 1.0 was used. For thorium and oxygen, we used the same basis sets as in our previous AE calculations on ThO.[1] A nuclear model of uniformly charged spheres[5] was assumed and atomic masses of 1.0, 16.0, 126.9, and 232.0 were used for hydrogen, oxygen, iodine, and thorium, respectively. The speed of light was taken to be 137.037 a.u.

We report three kinds of RFCA calculations (RFCA1, RFCA2, and RFCA3), in which we gradually reduce the size of the corelike basis functions, and also AE calculations for comparison. Table III shows the details of the basis sets formed by the atomic-balance scheme.[7,8] Table IV shows the total and valence orbital energies obtained by AE and RFCA calculations. The RFCA energies compare very well with the AE results, and reducing the sizes of the corelike bases appeared to have little effect.

B. Molecular total and valence orbital energies

Tables V and VI show the molecular total and valence orbital energies for HI and ThO at internuclear distances near their equilibrium bond lengths. We examined the effect of neglecting $(SS|SS)$ integrals over valence basis functions as described above. The RFCA calculations using this approximation are indicated by asterisks. We also examined the use of spectral representations (SR) for calculating the core Hamiltonian (CH) matrices. These are marked by ''s'' in the tables and will be referred to as SRCH hereafter. The spectral functions adopted for the calculations on HI were the

TABLE VI. Total energies (E) and valence orbital energies (ϵ) for ThO at internuclear distance of 3.48 a.u.

	$-E$	$-\epsilon(26e_{1/2})$	$-\epsilon(27e_{1/2})$	$-\epsilon(28e_{1/2})$	$-\epsilon(29e_{1/2})$	$-\epsilon(14e_{3/2})$
AE	26 585.637 08	0.929 34	0.481 38	0.458 84	0.217 91	0.475 38
RFCA1	26 585.636 91	0.930 56	0.479 97	0.457 73	0.218 49	0.474 09
RFCA1*	26 585.636 91	0.930 56	0.479 97	0.457 73	0.218 49	0.474 09
RFCA1s	26 585.645 45	0.930 13	0.478 49	0.461 60	0.218 61	0.471 82
RFCA2	26 585.627 52	0.930 37	0.480 09	0.457 83	0.218 41	0.474 24
RFCA2*	26 585.627 52	0.930 37	0.480 09	0.457 83	0.218 41	0.474 24
RFCA2s	26 585.636 05	0.929 90	0.478 59	0.461 74	0.218 52	0.471 94
RFCA3	26 585.613 95	0.931 38	0.478 75	0.456 44	0.217 77	0.473 40
RFCA3*	26 585.613 95	0.931 38	0.478 75	0.456 44	0.217 77	0.473 40
RFCA3s	26 585.622 50	0.930 90	0.477 19	0.460 43	0.217 88	0.471 10

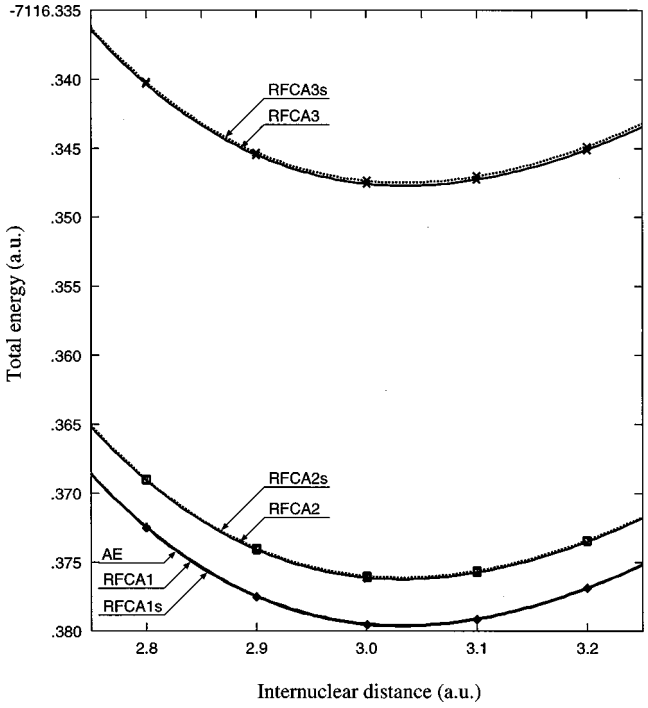

FIG. 1. Potential curves of HI.

atomic primitive Gaussians described in the previous subsection. For ThO, we tried various spectral functions, including the atomic basis functions for the AE and RFCA calculations.[1] The best results were obtained using even-tempered primitive Gaussians whose exponent parameters covered the range of those of the atomic basis functions.[1]

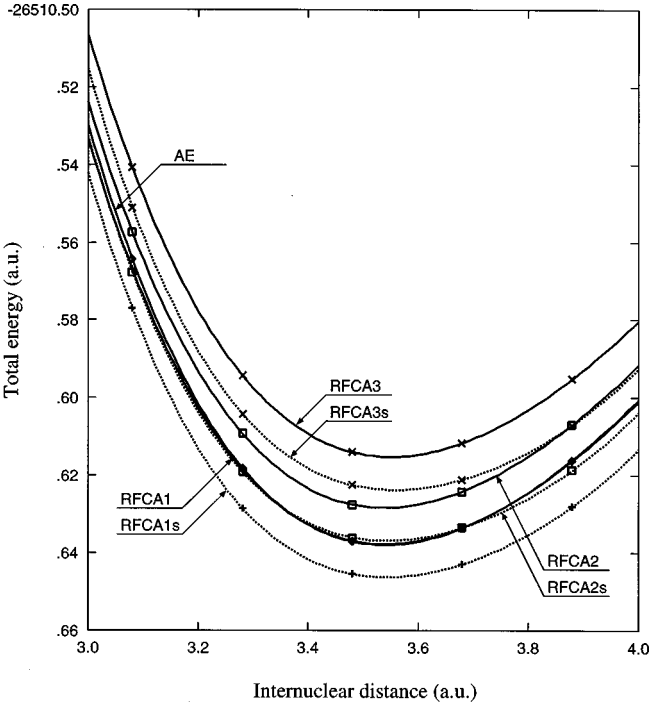

FIG. 2. Potential curves of ThO.

TABLE VII. Spectroscopic constants for HI and ThO.

		R_e[Å]	ω_e[cm^{-1}]	B_e[cm^{-1}]
HI	Expt	1.609	2309	6.426
	AE	1.604	2428	6.550
	RFCA1	1.605	2426	6.548
	RFCA1*	1.605	2426	6.548
	RFCA1*s*	1.604	2421	6.550
	RFCA2	1.605	2426	6.548
	RFCA2*	1.605	2426	6.548
	RFCA2*s*	1.604	2421	6.549
	RFCA3	1.606	2422	6.533
	RFCA3*	1.606	2422	6.533
	RFCA3*s*	1.606	2419	6.538
ThO	Expt.	1.840	896	0.333
	AE	1.874	938	0.321
	RFCA1	1.873	923	0.321
	RFCA1*	1.873	923	0.321
	RFCA1*s*	1.877	869	0.320
	RFCA2	1.873	923	0.321
	RFCA2*	1.873	923	0.321
	RFCA2*s*	1.876	869	0.320
	RFCA3	1.880	919	0.319
	RFCA3*	1.880	919	0.319
	RFCA3*s*	1.884	864	0.318

The Appendix gives details of the parameters. Similar results were obtained in the model potential calculations by Katsuki.[20]

The gradual decrease in the corelike basis sizes has a rather small effect on the energies. Neglecting $(SS|SS)$ integrals reproduces almost exactly the corresponding RFCA results, and thus could be safely adopted in all RFCA calculations. The SRCH works well for both HI and ThO.

C. Potential curves and spectroscopic constants

The total energies were calculated at several internuclear distances. Using four lower energies which bracketed the

TABLE VIII. Average computing time (in seconds) on IBM RS/6000 model 43P-133.

		1-elec.	2-elec.	SCF	Total
HI	AE	0.66	2800	1700	4500
	RFCA1	2200	2600	160	5000
	RFCA1*	2200	1300	160	3700
	RFCA1*s*	7.3	2600	160	2800
	RFCA2	1900	1600	160	3700
	RFCA2*	1900	800	160	2900
	RFCA2*s*	6.8	1600	160	1800
	RFCA3	1800	1200	160	3200
	RFCA3*	1800	580	160	2500
	RFCA3*s*	6.7	1200	160	1400
ThO	AE	2.1	57 000	15 000	72 000
	RFCA1	24 000	67 000	2200	93 000
	RFCA1*	24 000	36 000	1400	61 000
	RFCA1*s*	25	67 000	2200	69 000
	RFCA2	19 000	32 000	2200	53 000
	RFCA2*	19 000	17 000	1400	37 000
	RFCA2*s*	22	32 000	2200	34 000
	RFCA3	18 000	26 000	2200	46 000
	RFCA3*	18 000	14 000	1400	33 000
	RFCA3*s*	22	26 000	2200	28 000

TABLE IX. Even-tempered exponent parameters $\{\alpha\beta^i, i=0,...,(n-1)\}$ used for the spectral functions of ThO.

		α	β	n
Th	s	0.020 772 010	1.824 374 6	40
	p	0.060 000 000	1.835 422 4	34
	d	0.039 123 150	1.848 967 5	22
	f	0.059 087 000	1.822 998 2	17
O	s	0.285 577 66	1.853 525 2	24
	p	0.173 557 09	1.804 425 3	11
	d	1.154		1

points of minimum energy, the equilibrium bond lengths R_e, the harmonic frequencies ω_e, and the rotational constants B_e were evaluated. Figures 1 and 2 show the potential curves and Table VII gives the calculated and experimental[21] spectroscopic constants.

The RFCA potential curves are exactly the same as or almost parallel to those obtained by AE calculations. The calculations without $(SS|SS)$ integrals exactly reproduced the corresponding RFCA curves, and are therefore not shown in the figures. Thus, this approximation is justified and could always be adopted. The SRCH worked very well for HI. However, for ThO it gave harmonic frequencies that were somewhat different from those of the original RFCA calculations. It even gave somewhat lower total energies than the AE calculation, although the potential curves are almost parallel. These RFCA and AE calculations gave values that were comparable to experimental values.[21]

IV. DISCUSSION

All of the calculations were performed using an IBM RS/6000 model 43P-133 workstation. Table VIII shows an example of timing data shown by two significant figures. Since these are averages of several calculations and should depend on the programming algorithm and computer, the numerical values in Table VIII should be regarded only as indications. As expected, RFCA reduced the computing time required for two-electron integrals, and neglecting $(SS|SS)$ integrals reduced computing time by one half without any substantial loss of accuracy. However, these RFCA calculations still require considerable computing time to calculate one-electron integrals of core Hamiltonians, and the SRCH reduces this by a factor of about a hundred or a thousand. Unexpectedly, RFCA required one-tenth the SCF iteration time as AE calculations; the use of four-component basis functions in RFCA reduces the diagonalization time of Fock matrices. Thus, RFCA currently requires one half or one third of the total computing time needed for AE calculations.

Although the SRCH approximation gave rather good results for HI and ThO, in the numerical tests for other molecules it often gave results that were appreciably different than those obtained by AE and RFCA. Therefore, we think that the present SRCH method should be improved further before it can be safely adopted for any molecule; this is why we did not report the RFCA calculations using the SRCH without $(SS|SS)$ integrals. Improvement of the SRCH approximation will be investigated in future studies.

In conclusion, the proposed relativistic RFCA can reduce the required computing time and closely reproduce the results obtained by AE calculations, including total and valence orbital energies and spectroscopic constants. A further approximation by neglecting $(SS|SS)$ integrals involving only valence basis functions also works very well, but the SRCH approximation degrades the accuracy for some molecules.

APPENDIX

Table IX gives even-tempered Gaussian exponent parameters used for the spectral functions of ThO, as described in Sec. III B.

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