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Four-component relativistic configuration-interaction calculation using the reduced frozen-core approximation

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The reduced frozen-core approximation (RFCA) is a kind of frozen-core approximation (FCA). In our previous study [J. Chem. Phys. **109**, 8182 (1998)], we found that Dirac–Fock–Roothaan calculations using RFCA had some desirable features compared to the all-electron and usual FCA calculations. In this study, in addition to these features, we found that they also describe well unoccupied as well as occupied orbitals. We developed a fully relativistic multireference configuration-interaction (CI) program that incorporates these features of RFCA, and report CI calculations for ThO and AuH. The calculated spectroscopic constants agree well with experimental values. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1476694]

I. INTRODUCTION

The reduced frozen-core approximation (RFCA)[1,2] is a kind of frozen-core approximation (FCA) which treats valence electrons explicitly and core electrons as dormant in molecule formation. In the RFCA, the valence basis functions $\{\chi_p\}$ are Schmidt orthogonalized to core orbitals $\{\phi_c\}$ through *corelike* basis functions $\{\kappa_c\}$ to form core-orthogonalized valence basis functions $\{\omega_p\}$ as

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

where N_p is a normalization constant and $\{C_{cp}\}$ are coefficients to be determined so that $\langle\omega_p|\phi_c\rangle = 0$. The RFCA was proposed by one of the authors (O.M.)[1] for nonrelativistic Hartree–Fock–Roothaan calculations and later extended by us[2] to relativistic Dirac–Fock–Roothaan (DFR) calculations. In Eq. (1), the corelike basis functions κ_c were found[1,2] to have simpler forms than those of the corresponding core orbitals ϕ_c, so that the time needed to compute molecular integrals is less than with the usual FCA and all-electron (AE) calculations. The potential-energy curves in RFCA are shifted slightly upwards depending on the adopted corelike bases, but the spectroscopic constants in RFCA closely reproduce those determined by AE calculation. Furthermore, in the DFR calculation using RFCA,[2] four-component basis functions (double spinors) can be treated as units so that the self-consistent-field (SCF) iteration time is reduced. The RFCA can be regarded[1] as a mathematical rigorism of the model-potential method.[3–5]

In this article the RFCA is extended to a four-component relativistic configuration-interaction (CI) calculation to include electron correlation as well as relativistic effects. The relativistic CI method using RFCA is described in Sec. II, and the occupied and unoccupied orbitals in RFCA are examined in Sec. III. The DFR and relativistic CI calculations for ThO and AuH using RFCA are reported in Sec. IV. Conclusions on the RFCA are given in Sec. V. Throughout this article, atomic units will be used. The nucleus model of a uniformly charged sphere and a speed of light $c = 137.037$ a.u. are adopted for comparison with the previous article.[2]

II. RELATIVISTIC CONFIGURATION-INTERACTION METHOD USING THE REDUCED FROZEN-CORE APPROXIMATION

The relativistic RFCA adopted in this study is the same as that in the previous paper.[2] A salient feature is that the four-component molecular orbitals (MOs) $\{\phi_i\}$ are expanded in terms of the four-component core-orthogonalized valence basis functions $\{\omega_p\}$ in Eq. (1) as

$$\phi_i = \sum_p \omega_p C_{pi} \tag{2}$$

and the scalar coefficients $\{C_{pi}\}$ are optimized by the SCF iterative process. The matrix of the core Hamiltonian over the basis functions was computed exactly without using the spectral representation.[2]

Using these MOs, various configuration state functions (CSFs) are formed:

$$\Phi_I(1,2,\ldots,n) = (n!)^{-1/2}\det|\phi_{I1}(1)\phi_{I2}(2)\cdots\phi_{In}(n)| \tag{3}$$

and the n electron molecular wave functions are written as

$$\Psi(1,2,\ldots,n) = \sum_I \Phi_I C_I. \tag{4}$$

The coefficients $\{C_I\}$ and total energy E are determined by solving the eigenvalue equation:

$$\mathbf{Hc} = E\mathbf{c}, \tag{5}$$

where $\mathbf{c}$ is a column vector of coefficients $\{C_I\}$ and Hamiltonian matrix $\mathbf{H}$ consists of elements,

$$H_{IJ} = \langle\Phi_I|\hat{H}|\Phi_J\rangle, \tag{6}$$

where $\hat{H}$ is a Dirac–Coulomb molecular Hamiltonian.

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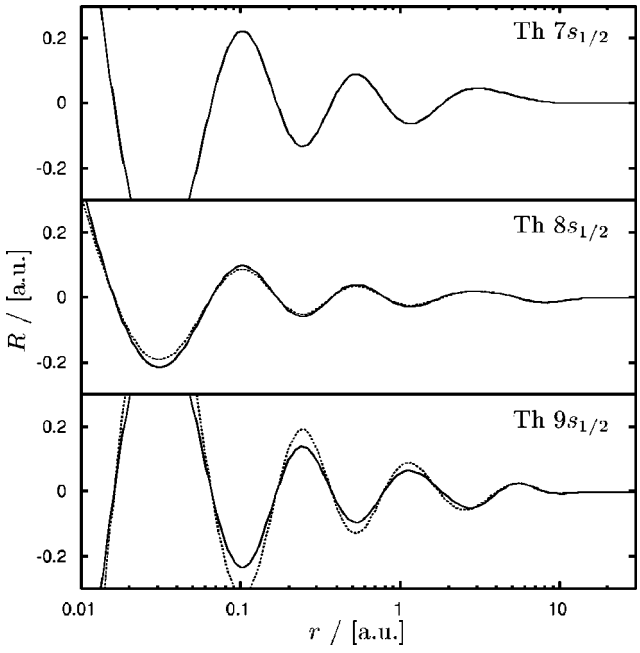

FIG. 1. Radial parts, R, of large-component $s_{1/2}$ orbitals of Th atom along radial distance r. Solid lines in AE calculation and dotted lines in RFCA calculation.

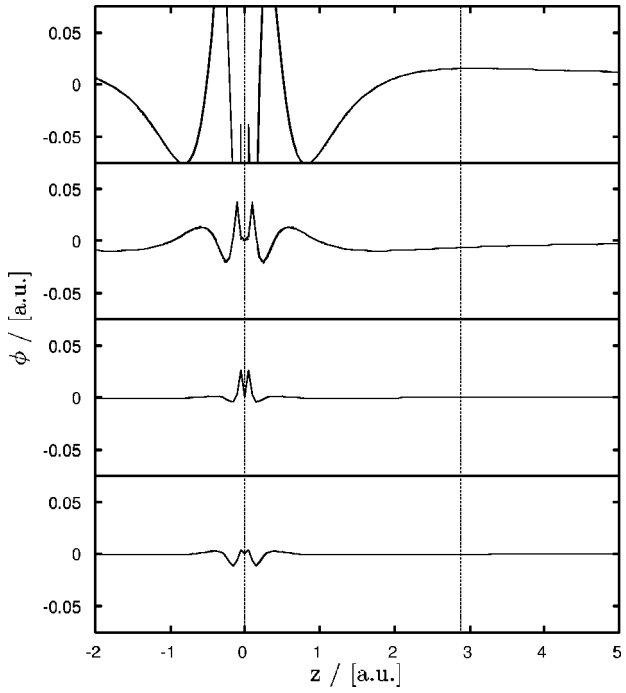

FIG. 2. The highest occupied orbital of AuH, ϕ, along bond axis. Top panel: The first large component. Bottom panel: The fourth small-component. Au atom on the origin and H atom on the z axis of 2.88 a.u. apart from the origin. Solid lines by AE calculation and dotted lines by RFCA calculation.

A relativistic CI method was formulated by Esser[6] using the unitary-group approach[7] and a relativistic CI program for general molecules was developed by Visscher *et al.*[8]

In this study, we developed a relativistic multireference CI program for linear molecules. The restriction to linear molecules has some merits; MO coefficients $\{C_{pi}\}$ in Eq. (2) and molecular integrals over atomic-orbital and MO bases are real, and a CSF consists of one Slater determinant as Eq. (3). Our CI calculation follows rather standard steps:

(1) A reference DFR wave function is obtained using RFCA.[2]
(2) Integrals over occupied and unoccupied MOs are computed.[9]
(3) To solve the eigenvalue equation (5), the direct CI method[10] combined with Davidson's diagonalization method[11,12] is used.

To compute the Hamiltonian matrix, Eqs. (5) and (6), (or more exactly **Hc** vector) the unitary-group approach[7] or the symbolic matrix method[13] is usually used. In our program we adopt a rather naive and direct Slater–Condon rule[14–16] to evaluate matrix elements between Slater determinants. Furthermore, using the molecular integrals stored in fast memories, we calculate the elements of the Hamiltonian matrix every time as they are needed. This method would require slightly more computing time. However, the program is very easy to code. Numerical experience has shown that a CI eigenvalue equation of about one million dimensions can actually be solved if we pay attention to the proper use of large fast memories. The details are described elsewhere.[17]

III. VALENCE ORBITALS IN THE REDUCED FROZEN-CORE APPROXIMATION

Since CI wave functions in RFCA are expressed in terms of occupied and unoccupied valence orbitals, it would be desirable for the orbitals in RFCA to closely resemble those in AE calculations. Thus, we examined this point for several atoms and molecules.

As the first example, Fig. 1 shows the radial parts of large-component orbitals of a Th atom in RFCA and AE DFR calculations obtained using RFCA2 and AE basis sets in the previous article.[2] The highest occupied $7s_{1/2}$ orbital in

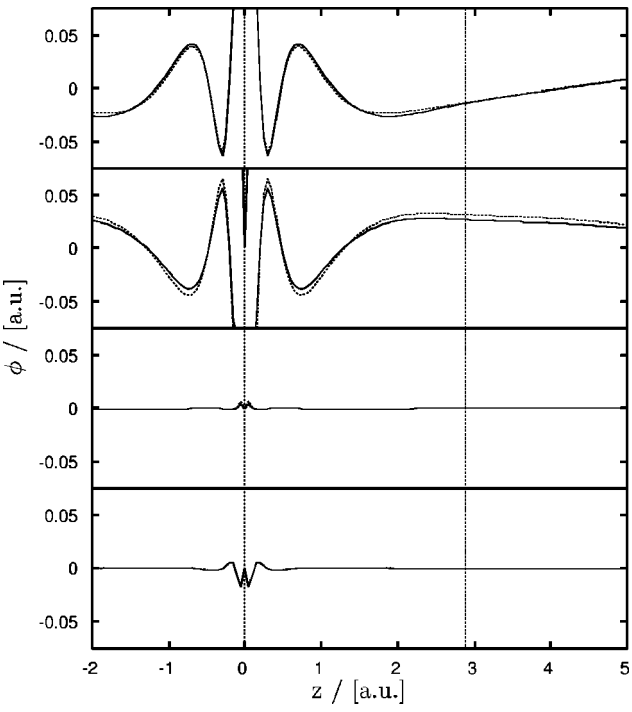

FIG. 3. The lowest unoccupied orbital of AuH.

TABLE I. Basis sets for AE and RFCA calculations. Basis set contractions are 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 total energy	−0.499 82	−0.499 82	−0.499 82	−0.499 82
$s+$	$5/1^5$	$5/1^5$	$5/1^5$	$5/1^5$
$p-,p+$	1/1*	1/1*	1/1*	1/1*
O total energy	−74.820 0		−74.819 6	−74.817 2
$s+$	$10/4,1^6$		$9/\underline{4},1^5$	$8/\underline{3},1^5$
$p-,p+$	$6/3,1^3$		$6/\underline{3},1^3$	$6/\underline{3},1^3$
$d-,d+$	1/1*		1/1*	1/1*
Au total energy	−19 035.4724	−19 035.4725	−19 035.4705	−19 035.4725
$s+$	$24/4,1^{20}$	$24/\underline{10},\underline{3},\underline{2},\underline{3},\underline{2},1^4$	$21/\underline{7},\underline{3},\underline{2},\underline{3},\underline{2},1^4$	$24/\underline{10},\underline{3},\underline{2},\underline{3},\underline{2},1^4$
$p-$	$21/4,2,1^{13},1^{*2}$	$21/\underline{10},\underline{3},\underline{2},1^4,1^{*2}$	$18/\underline{7},\underline{3},\underline{2},1^4,1^{*2}$	$21/\underline{10},\underline{3},\underline{2},1^4,1^{*2}$
$p+$	$21/4,2,1^{13},1^{*2}$	$21/\underline{11},\underline{2},\underline{3},1^3,1^{*2}$	$16/\underline{6},\underline{2},\underline{3},1^3,1^{*2}$	$21/\underline{11},\underline{2},\underline{3},1^3,1^{*2}$
$d-,d+$	$15/4,2,1^9$	$15/\underline{7},\underline{3},1^5$	$13/\underline{5},\underline{3},1^5$	$15/\underline{7},\underline{3},1^5$
$f-,f+$	10/10	10/10	10/10	$10/\underline{10}$
Th total energy	−26 510.5611		−26 510.5544	−26 510.5421
$s+$	$24/5,2,1^{17}$		$19/\underline{6},\underline{2},\underline{2},\underline{2},\underline{2},\underline{2},1^3$	$17/\underline{4},\underline{2},\underline{2},\underline{2},\underline{2},\underline{2},1^3$
$p-$	$20/6,1^{13},1^*$		$16/\underline{6},\underline{2},\underline{2},\underline{2},\underline{2},1^3,1^*$	$16/\underline{6},\underline{2},\underline{2},\underline{2},\underline{2},1^3,1^*$
$p+$	$20/6,1^{13},1^*$		$14/\underline{4},\underline{2},\underline{2},\underline{2},\underline{2},1^3,1^*$	$14/\underline{4},\underline{2},\underline{2},\underline{2},\underline{2},1^3,1^*$
$d-$	$16/3,3,1^{10}$		$13/\underline{4},\underline{2},\underline{3},1^4$	$12/\underline{3},\underline{2},\underline{3},1^4$
$d+$	$16/3,3,1^{10}$		$13/\underline{4},\underline{2},\underline{3},1^4$	$11/\underline{2},\underline{2},\underline{3},1^4$
$f-,f+$	$12/8,1^{*4}$		$9/\underline{5},1^{*4}$	$9/\underline{5},1^{*4}$

RFCA does not differ from the corresponding one in the AE calculation. The unoccupied $8s_{1/2}$ and $9s_{1/2}$ orbitals in RFCA slightly deviate from those in the AE calculation but the positions of their nodes and peaks agree with those in the AE calculation.

As a second example, Figs. 2 and 3 show the highest occupied $23e_{1/2}$ and the lowest unoccupied $24e_{1/2}$ MOs of AuH along the Au–H bond. The Au atom is placed at the origin and the H atom on the z axis at 2.88 a.u. from Au. The Au basis sets used are those for AE and RFCA1 in Table I[18] and the H basis set is the same as that in the previous work.[2] As in the Th atom, the occupied MO in RFCA closely resembles the corresponding one in the AE calculation while the unoccupied MO in RFCA slightly deviates from the MO in the AE calculation, although the positions of the nodes and peaks agree with those in the AE calculation.

These results and several other calculations indicate that RFCA can be safely adopted in CI calculations.

IV. RESULTS AND DISCUSSION

To determine the role of the relativistic effect and electron correlation, we performed DFR and relativistic CI calculations for some molecules. We report here the results for ThO and AuH.

A. ThO

This molecule was studied previously[2] in the framework of single-determinant DFR calculations using RFCA. In the present study, to determine the effect of electron correlation, we also performed relativistic CI calculations. The basis sets previously adopted[2] for Th and O were also adopted here, and are shown in Table I. The basis sets used for AE and RFCA calculations are named AE and RFCA, respectively. The RFCA2 basis for Th differs from the RFCA3 with regard to the size of the s- and d-type corelike basis functions. The reference E_0 ground-state configuration is

TABLE II. Numbers of core orbitals (N_{core}), valence occupied orbitals (N_{val}), and unoccupied orbitals (N_{unocc}) resulting from the use of basis sets of Table I.

	ThO(RFCA2/RFCA3)[a]			AuH(RFCA1/RFCA2)[a]			AuH(RFCA3)[a]		
	N_{core}	N_{val}	N_{unocc}	N_{core}	N_{val}	N_{unocc}	N_{core}	N_{val}	N_{unocc}
$e_{1/2}$	23	6	36	15	7	27	17	5	27
$e_{3/2}$	12	2	24	7	5	13	9	3	13
$e_{5/2}$	5	0	13	2	3	4	4	1	4
$e_{7/2}$	1	0	4	0	1	0	1	0	0
Total	41	8	77	24	16	44	31	9	44

[a]Basis sets of Table I.

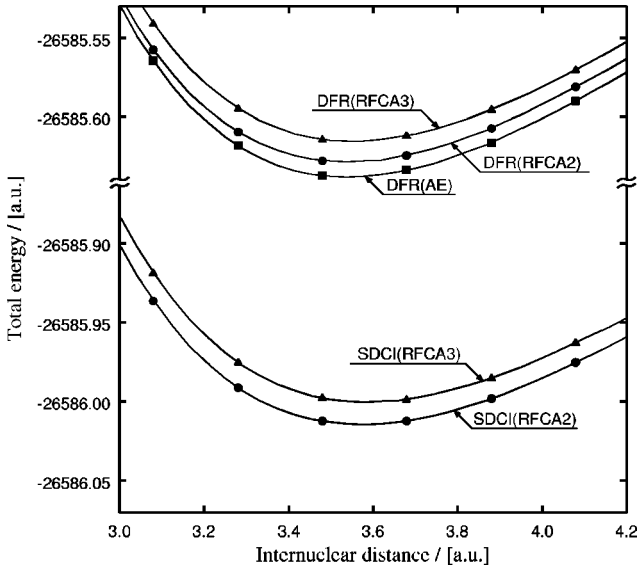

FIG. 4. Potential-energy curves for E_0 ground state of ThO.

$(29e_{1/2})^2(14e_{3/2})^2(5e_{5/2})^2(1e_{7/2})^2$, where only the highest occupied orbitals of each symmetry are explicitly shown. The sizes of MO spaces resulting from the use of basis sets, RFCA2 and RFCA3, are shown in Table II. Thus, when we use these basis sets, the occupied valence and unoccupied orbital spaces consist of 8 and 77 MOs, respectively. In the CI calculations, we included all single and double (SD) excitations from these 8 occupied valence orbitals to all of the unoccupied MOs. The CI dimension of this SDCI calculation was 219 189.

Figure 4 shows the potential-energy curves of the E_0 ground state obtained by DFR and CI calculations. The basis sets used,[2] AE, RFCA2, and RFCA3, are given in parentheses. These curves show that, as anticipated, the electron correlation lowers the total molecular energies, and the RFCA curves are almost parallel to each other.

Using four lower energies that bracketed the points of minimum energy, the equilibrium bond length r_e, the harmonic frequencies ω_e, and the rotational constants B_e were evaluated. The dissociation energies D_e were also calculated using the minimum total energies at r_e's and the total energies at a Th–O bond distance of 1000 a.u. Table III shows the calculated spectroscopic constants, and compares them with experimental values[19] and the results of quasirelativistic pseudopotential (QRP) calculations by Küchle *et al.*[20] The DFR results for r_e and B_e are almost the same as those by CI calculations, while the results for ω_e and D_e deviate somewhat from those by CI. The results of SDCI calculations are comparable to those of QRP(CASSCF+MR-SDCI) calculations[20] and experimental values,[19] which indicates the importance of electron correlation.

B. AuH

This molecule has been studied by many investigators, as seen in RTAM books by Pyykkö[21] and a recent article by Schwerdtfeger *et al.*[22] In this study, we performed DFR and single-reference (SR) and multireference (MR) CI calculations. The basis sets used for Au are taken from Okada and Matsuoka[18] and are shown in Table I. Two diffuse p-type basis functions were added as polarization functions. The RFCA3 basis set differs from RFCA1 in that the f-type basis functions in the latter are now regarded as core orbitals. The H basis set is the same as that used previously.[2]

TABLE III. Spectroscopic constants for ground state of ThO.

	r_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})	D_e (eV)
Expt.[a]	1.840	896	0.333	9.06, 8.85
Küchle *et al.*[b]				
SCF	1.829	943		6.07
SCF+CI(SD)	1.865	911		8.06
CASSCF+MRCI(SD)	1.884	870		8.48
Present study				
DFR(AE)	1.874	937	0.320	7.61
DFR(RFCA2)	1.873	923	0.321	7.55
DFR(RFCA3)	1.879	919	0.318	7.41
SDCI(RFCA2)	1.891	892	0.315	8.48
SDCI(RFCA3)	1.897	888	0.313	8.33

[a]Experimental value (Ref. 19).
[b]Quasirelativistic pseudopotential calculations (Ref. 20).

We first performed DFR calculations for the E_0 ground state configuration $(22e_{1/2})^2\ (12e_{3/2})^2\ (5e_{5/2})^2\ (1e_{7/2})^2$. The potential-energy curves are shown in Fig. 5. As seen in ThO and other molecules,[2] the RFCA curves shift upwards but are almost parallel to each other and to the AE curve. The spectroscopic constants are given in Table IV. The RFCA constants are almost the same as the AE constants but the calculated ω_e and B_e deviate a little from the experimental values.[19]

To determine the role of electron correlation, we then performed SR CI calculations including all SD excitations of valence electrons (i.e., SR-SDCI). In DFR calculations, we previously found that the $4f$ orbitals of Au did not take part in chemical binding. Thus, we performed two kinds of SDCI calculations on E_0 states; in SDCI (RFCA1/RFCA2) calculations, the $4f$ orbitals of Au were treated as valence orbitals

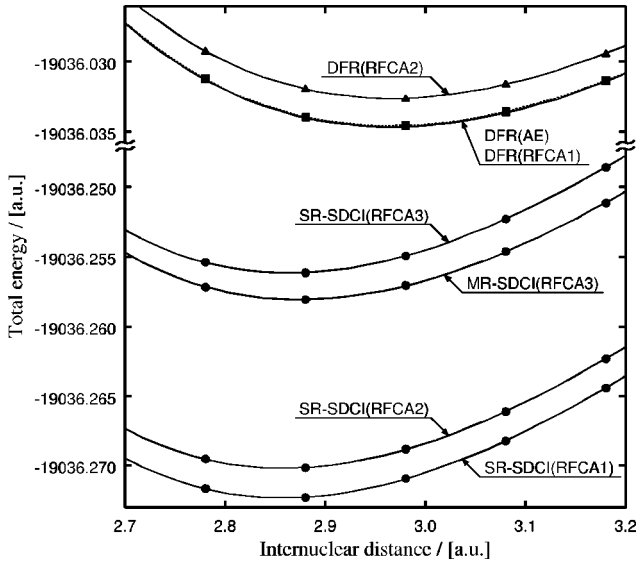

FIG. 5. Potential-energy curves for E_0 ground state of AuH.

TABLE IV. Spectroscopic constants for ground state of AuH.

	r_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})	D_e (eV)
Expt.[a]	1.524	2305	7.240	3.36
Dyall[b]				
DFR	1.570	2067		1.78
DFR/MP2	1.497	2496		3.11
Schwerdtfeger *et al.*[c]				
DFR	1.570	2095		1.79
DFR/MP2	1.484	2521		3.21
PP	1.574	2068		1.70
PP/MP2	1.479	2522		3.14
Witek *et al.*[d]				
RESC/MRMP	1.495	2412	7.52	2.87
Present study				
DFR(AE)	1.569	2103	6.828	
DFR(RFCA1)	1.569	2101	6.824	
DFR(RFCA2)	1.570	2101	6.823	
SR-SDCI(RFCA1)	1.512	2295	7.351	
SR-SDCI(RFCA2)	1.512	2294	7.349	
SR-SDCI(RFCA3)	1.515	2292	7.321	
MR-SDCI(RFCA3)	1.521	2258	7.267	3.03

[a]Experimental value (Ref. 19).
[b]Reference 23.
[c]DFR method and relativistic pseudopotential (PP) method (Ref. 22).
[d]Relativistic elimination of small components (Ref. 24).

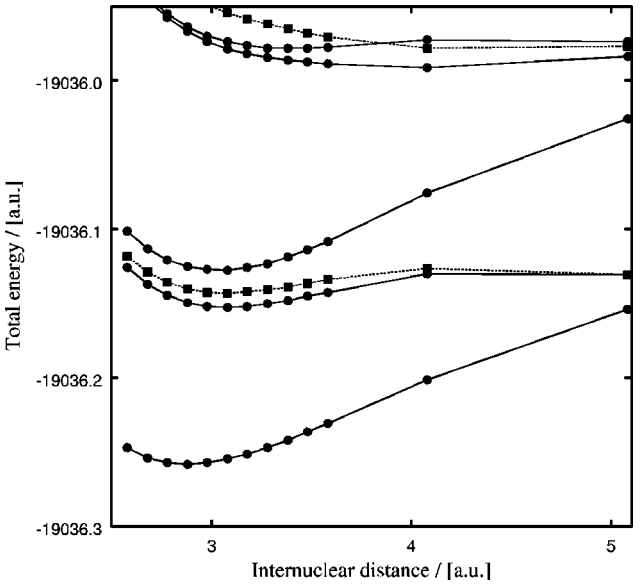

FIG. 6. Potential-energy curves for E_0 and E_1 states of AuH obtained by the MR-SDCI(RFCA3) and SR-SDCI(RFCA3) calculations. Solid lines are E_0 states and dotted lines E_1 states.

while in SDCI(RFCA3) calculations they were regarded as core orbitals (also see Table II). The CI dimensions were 261 419 and 96 219, respectively. Figure 5 compares the potential-energy curves of the E_0 ground state. As seen in the DFR calculations, they are almost parallel to each other. Table IV shows the spectroscopic constants. The dissociation energies D_e were calculated using the minimum total energies at r_e's and the total energies at a Au–H bond distance of 30 a.u. Again, each of these SR-CI calculations gave spectroscopic constants that agreed well with experimental findings,[19] except for D_e. These results also show that the $4f$ orbitals of Au can be safely regarded as core orbitals.

To improve D_e, we then performed MR-SDCI calculations in which we took three reference E_0 states: the DFR ground state,

$$(22e_{1/2,1/2})^1(23e_{1/2,-1/2})^1(12e_{3/2})^2(5e_{5/2})^2(1e_{7/2})^2$$

and

$$(22e_{1/2,-1/2})^1(23e_{1/2,1/2})^1(12e_{3/2})^2(5e_{5/2})^2(1e_{7/2})^2.$$

The two added CSFs describe single excitations from the highest occupied MO, $22e_{1/2}$, to the lowest unoccupied MO, $23e_{1/2}$. We used the RFCA3 basis set of Au in which the $4f$ orbitals are regarded as cores. The CI dimension was 259 741. The calculated D_e now compares well with the experimental findings.[19]

Figure 6 shows the potential-energy curves of the E_0 ground and some excited states obtained by MR-SDCI calculations. It also depicts some E_1 excited states by SR-SDCI calculations in which the reference configuration is $(22e_{1/2,1/2})^1(23e_{1/2,1/2})^1(12e_{3/2})^2(5e_{5/2})^2(1e_{7/2})^2$. Table V shows the spectroscopic constants for lower excited E_0 and E_1 states calculated using these potential-energy curves and compares them with a two-component relativistic MR perturbation-theory calculation by Witek *et al.*[24] The excitation energies from the ground state, T_e, by the SR-SDCI calculations are comparable to their findings[24] for the E_1 state [i.e., 1(I)] but are larger than those for the E_0 states [i.e., 0^-(I) and 0^+(II)]. The latter discrepancy is greatly improved by the MR-SDCI calculations.

V. CONCLUSION

The RFCA is a kind of FCA that adopts core-orthogonalized valence basis functions through *corelike* basis functions. DFR calculations using RFCA have the following features.

(1) The time needed to compute molecular integrals is reduced compared to the usual FCA and AE calculations.

(2) Four-component basis functions can be treated as units, which reduces the SCF iteration time.

TABLE V. Spectroscopic constants for lower excited states of AuH.

State		T_e (eV)	r_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})
0^-(I)	RESC/MRMP[a]	3.18			
	SR-SDCI(RFCA3)[b]	7.14			
	MR-SDCI(RFCA3)[b]	2.88			
1(I)	RESC/MRMP[a]	3.19			
	SR-SDCI(RFCA3)[b]	3.13			
0^+(III)	Expt.[c]	3.43	1.673	1670	6.007
	RESC/MRMP[a]	3.20	1.592	2059	6.63
	SR-SDCI(RFCA3)[b]	7.63	1.719	1627	5.689
	MR-SDCI(RFCA3)[b]	3.55	1.606	2183	6.521

[a]Relativistic elimination of small components (Ref. 24).
[b]Present study.
[c]Experimental value (Ref. 19).

(3) They can reproduce well the spectroscopic constants obtained by AE calculations, although their potential-energy curves are shifted slightly upwards depending on the corelike bases used.

(4) They can closely describe occupied and adequately describe unoccupied orbitals.

To include electron correlation as well as relativistic effects, a relativistic MR CI program for linear molecules has been developed. It incorporates the above-mentioned features of RFCA and the characteristics of linear molecules. SR-SDCI and MR-SDCI calculations using RFCA gave spectroscopic constants that agreed fairly well with experimental values. Hence, relativistic CI calculations using RFCA add a feature of RFCA.

(5) They can well describe both relativistic effects and electron correlation.

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